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CONTEMPORARY CHEMISTRY

CONTEMPORARY CHEMISTRY

A SURVEY OF THE PRESENT STATE, METHODS AND TENDENCIES OF CHEMICAL SCIENCE

BY

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PREFACE

THE following pages are intended to give a bird's-eye view of the whole field of modern chemistry. A subject distinguished for the diversity of its methods and the isolation of many of its important results is one which naturally presents considerable difficulties to any attempt at a concise summing-up. But a readable summary, however inadequate, is so obviously desirable in the interests of chemistry and (more especially) its allied sciences that the author has ventured to essay the task with such assistance as the excellent chemical publications of the day and the kindness of some of the acknowledged leaders of chemical research placed at his disposal.

The aim throughout has been to include the latest phase of each subject, down to the end of 1910. Where new terms and conceptions have arisen, these are defined and explained, so as to bridge the gap between the chemical teaching of the last generation and the schools of the present day.

Special attention has (largely for personal reasons) been paid to physical chemistry and to current attempts at physical and electrical theories of chemical phenomena, in the belief that such theories bear within them the germs of future discoveries. The forecasts of future developments which have been occasionally indulged in must be taken as the author's private views only. Though liable to unexpected deviations, they may be found useful as indicating some of the directions in which chemical research is likely to advance in the near future.

E. E. FOURNIER D'ALBE.

THE UNIVERSITY, BIRMINGHAM,
January, 1911.

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CONTEMPORARY CHEMISTRY

CHAPTER I

THE SITUATION

THE aim of science is to interpret all nature in terms of our own familiar sensations and activities. In astronomy we measure and weigh the heavenly bodies as with a yard and balance, and swing them round in their orbits by forces differing only by a numerical factor from the force we are ourselves capable and conscious of exerting. In geology, we lay down the earth's surface in successive strata, water them with rain, grind them with ice, sow them with the seeds of life, crumple them up, and pass them through a volcanic furnace. In physics we deal with bodies comparable, in their three states of aggregation, to our own bones, blood, and breath, and study their behaviour under the influence of the various stimuli to which we ourselves are accustomed to respond. In biology, we investigate the circumstances of lives like our own, and proceed to structures more and more remote from ourselves, until the analogies are reduced to the two fundamental motives which, according to Schiller, keep the world-machine in motion—hunger and love. And when those characteristics fail us, when the number of organisms becomes too vast and their size too minute to enable us to detect anything but blind chance in their life-history, then we enter the domain of Chemistry.

"It is really impossible," says Sir William Ramsay, "to manipulate quantities of the order of a few tenths of a milligram."* Yet a tenth of a milligram, even of the heaviest element, contains at least half a trillion ($0{\cdot}5 \times 10^{18}$) atoms. As chemistry, properly so called, deals only with tangible substances, which can be "manipulated," it follows that all purely chemical methods work with aggregates of units numbering over a million times the number of individuals in the whole human race. The populations of Australasia, America, Africa, Europe, and Asia form approximately a geometrical progression of the form 1, 2, 4, 8, 16. Imagine the teeming millions of China and India, the hordes of Africa, and the civilised populations of Europe and America lumped together and multiplied a millionfold—men, women, and children, and the whole aggregate subjected to some supra-chemical analysis. What would be the result?

The "substance" would turn out to be an "element." No amount of interaction with other masses of a different species would split it up into two or more independent substances. Hence the efforts of the supra-chemist would be necessarily confined to an investigation of its physical properties, and its ultimate structure.

And, firstly, there would be the three states of aggregation. In the "liquid" state of humanity the "atoms" would constantly remain within each other's sphere of influence, within hail or signalling distance. They would exhibit a good deal of cohesion and of what we have lately come to call "steric hindrance." When scattered beyond that distance the human units or atoms would act more or less independently, but always retain a tendency to form binary groups or higher "molecular" associations. A tightly packed crowd would resemble a viscous and rather amorphous solid. A tendency to crystallisation would be shown in the slow deposit of an orderly audience at a place of entertainment. At the "absolute zero of temperature," illustrated by the graveyard, there would be evidence of crystallisation in a quadratic system. And even the phenomena of Lehmann's "living crystals" would be paralleled by an army on the march.

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* Presidential Address to the Chemical Society, 1909. He has since then brought a balance into use which is capable of weighing a 500,000th of a milligram. See p. 101 below.

These phenomena could not, however, be properly observed unless the quantity of material were greatly increased. Yet, even with a very small amount of material, some physical properties may be observed with ease. Many physical reactions are much more delicate than any chemical reactions. Spectroscopy, ultra-microscopy, and radio-activity have brought us within measurable distance of the molecule, or even the atom. Thus might our supra-chemist make deductions from the rhythm of a marching regiment, from the appearance of minute social aggregates, or from the birth-rate. One of the difficulties he would have to contend with would be that the human race is practically a two-dimensional structure, confined, like the film of a soap-bubble, to the outer surface of a sphere, and only paralleled in modern chemistry by the excessively thin films of radio-active deposits. His "deci-milligram" of human material would not fit on the earth's surface unless arranged in some twenty layers, and closely packed. His difficulties in arriving at an intelligible scheme of the structure of such a mass are closely paralleled by the difficulties which beset all ultimate chemical theories.

Considering these difficulties, it is both surprising and creditable that so much progress has been made already towards the unravelling of the knotty constitution of matter. A number of fundamental laws stand out like beacon-lights to illumine the chaos of phenomena. They bear the names of Dalton, Avogadro, Dulong and Petit, Regnault, Boyle, Mariotte, Gay-Lussac, Graham, Gibbs, Raoult, Van't Hoff, Arrhenius, and a number of even more recent discoverers. They form the Code Napoléon of the empire of chemistry.

What is nowadays the greater division of chemistry is ruled by the atom of Carbon. There, if anywhere, is the reign of law and order. Organic chemistry resembles a state which enjoys an admirable staff of police. The carbon atoms keep order everywhere. Their fourfold valency has withstood the most severe forms of chemical torture. The great homocyclic division of organic chemistry is ruled by that most fascinating of oligarchies, the Benzene Nucleus, whose hexagonal symbol pervades and perfumes every modern organic text-book. Yet it is just here that chemical theory altogether transcends the grasp of the physicist. We are asked to imagine the carbon atom in the form of a rigid tetrahedron, carrying a valency, like a small hook, at each of its four corners. Such tetrahedra form rings, chains, and more complicated structures. And then the organic chemist turns round to the physicist and asks him kindly to render such structures into the language of the electron theory!

The physicists reply with a *non possumus.* Sir Joseph Thomson compromises by constructing an atom of a nebulous kind of positively electrified stuff inside which electrons revolve in concentric rings or shells. He calls upon chemists to work that conception into their formulæ and crystallographies. Sir William Ramsay and his acolytes take up the challenge, and reconstruct the system of the elements from Prout's whole numbers by adding or subtracting so many rings of electrons.

While those two great neo-alchemists are endeavouring to meet on the common ground of transmutation from the theoretical and practical sides respectively, the bulk of the chemical army is doing spade-work. What else can they do? While the physicist can always soar into the higher realms of mathematics, the chemist is encumbered with an *embarras de richesse* of substances to which his colleagues are adding new ones every day. Many of these, indeed, fit into schemes previously conceived. Their discovery is often the direct result of such schemes. But, as often as not, a hardly-won generalisation is discredited by the behaviour of the latest product of organic synthesis, and the search for the much-needed law has to commence over again. The frequent recurrence of such a calamity has covered chemical theorising with a somewhat unmerited reproach. Theories are just what chemistry wants most. They are also what chemists seem least able or inclined to make for themselves. They look to the physicist to do it for them. The extraordinary prestige which the electron theory enjoys among chemists is largely due to this attitude.

Now, I do not wish to minimise the importance of the electron theory. It covers effectively the whole ground of electricity and magnetism, and is in a fair way of absorbing also the science of optics. But we are as yet very far indeed from an electron theory of Chemistry. And when that theory is formulated, it is quite possible that our ideas of the electron may be, if not considerably modified, at least highly specialised by the light which chemical facts may throw upon it.

To give some illustrations. Those substances in which the electron plays the most obscure part are the insulating carbon compounds. Yet it is just these in which the greatest chemical regularities are observed. Inorganic chemistry, to which, by the way of electrolysis, the new theory of electricity has first been applied, is really the most chaotic field of modern chemistry. We do not yet actually know whether chlorine has eight valencies or only one, and an equally hopeless diversity of opinion obscures the true nature of peroxides. And even that most successful and fruitful application of ionic conceptions, the theory of solutions, suffers under the rivalry of four different theories of osmotic pressure, based respectively on gas pressure, surface tension, hydrates, and vapour pressure.

The rock ahead of any electron theory of chemistry is Crystallography. The electron theory has familiarised us with the conception of an atom as a sort of Solar System, with asteroidal or Saturnian rings, and a generally ethereal structure. Crystallography, on the other hand, brings us face to face with "solid reality" in the shape of structures of marvellous regularity, exhibiting all the characteristics of a true architecture of solid and identical bricks. Molecular theories of the older school of physics teach us that the molecules of these crystallised substances are in actual contact. Such contact is difficult to imagine unless we have solid molecules and atoms to start with. Moreover, such solid ultimate structure is also required by the sudden incompressibility acquired by a body on entering the liquid or solid state.

The science of crystallography is independent of physics to a remarkable extent. Since Bravais constructed his "space-lattices" from purely geometrical considerations, other crystallographers have evolved 230 possible systems of points, each consisting of identical arrangements or their mirror-images, and mineralogists have discovered actual specimens illustrating most of these numerous point systems. The pure elements, on the other hand, crystallise either in the cubic or hexagonal systems, which give the closest possible packing in three-dimensional space of a system of equal spheres. Again, it has been suggested that if atoms are elastic spheres possessing mutual attraction, that attraction will, in the solid state, produce an internal pressure which will convert the spheres into polyhedra, and give us something like a honeycomb structure.

All this has to be taken into account when we want to formulate an intimate theory of the constitution of matter.

The new science of Chemical Physics forms a neutral ground on which physicists and chemists may meet and co-operate. Such co-operation is becoming more and more desirable. The department of Physics is anxious for new substances on which to try its newly discovered laws, and test its widest theories. Chemistry, on the other hand, is emitting a steady stream of facts, ill-assorted and obscure indeed, but bearing the ennobling stamp of truth.

The following chapters are intended as a survey of the whole ground of modern chemical work with a view towards this physico-chemical co-operation. It is proposed to outline the laws, conceptions, and ideals underlying the new chemistry, to show where they are at variance with Physics, and where the bridge between the two sciences has already been thrown. It is inevitable that the point of view, and, possibly, the prejudice, of the physicist may sometimes obtrude itself; but the chemical expert will no doubt forget this over the new experience of "seeing himself as others see him."

CHAPTER II

A RETROSPECT

We have travelled far and fast since the Sacred Art was born on the banks of the Nile. The inscriptions at Edfu and Dendera prove that chemical laboratories were attached to the temples, and that the precious and profitable secrets of metallurgy, medicine, and glass-blowing were jealously restricted to select initiates. Yet the treasures of knowledge could not be for ever hidden. Even the Jews took with them more valuable spoil than Egyptian trinkets, in the shape of an acquired knowledge of various arts and crafts; and when wise men came from the Grecian world, Solon, Pythagoras, Herodotus, Plato, they garnered much priceless information from their too communicative and hospitable hosts.

But the Greek genius despised handicrafts. The Greek philosopher preferred wearing the purple dye in his academical peripatetics to sweltering at the dyeing-vat, or laboriously extracting the coloured juice from the root of the madder plant. The Greek artist, indeed, used white-lead, cinnabar, vermilion, cobalt, verdigris, iron rust, and soot for his mural paintings. The scribe made an ink of soot and gum. But it does not seem to have occurred to anybody to solve the problems of Nature by questioning Nature herself. Even the transcendent genius of an Archimedes was confined to such problems as could be brought within the magic circle of geometry, where the deductive method ruled supreme.

If the word "chemistry" (Greek, "chemeia") is derived from Chem or Cham, the old Egyptian name for Egypt itself, it is not surprising that both the old metallurgy and the latter alchemy should have found their first home there. It was the Alexandrian merchants who, when Alexandria had become the world's chief emporium, began to tamper with the coinage, and "dyed" their debased gold as far back towards the original colour as their knowledge of alloys would permit. When the "philosophers" took up the pursuit, they probed somewhat deeper, and instead of merely dyeing or "tinting" the baser metals to the colour of gold, they endeavoured to change their very nature. In this endeavour they had, as they held, both reason and experience at their back. Aristotle recognised four "elements"—earth, water, air, and fire. To these the Indian sages added two more, ether and consciousness. The Greek philosophers were not quite clear whether an element meant more than a mere property, which is much as if to say that a thing "is" what it seems to be. Aristotle, indeed, went a little farther and reduced his four elements to the presence or absence of two qualities—to wit, heat and moisture—just those things which we recognise at the present day as the first requisites of organic life. The scheme worked as follows:—

Cold and dry: Earth.
Cold and moist: Water.
Warm and moist: Air.
Warm and dry: Fire.

Each element could be transmuted into another by adding or subtracting heat or moisture, and natural processes were taken as so many illustrations of these metamorphoses.

Little wonder, then, that it was thought possible to change silver and copper into gold, and that there was a widespread belief, both in China and in the Mediterranean, that such transmutation had often been accomplished. Did not the Emperor Diocletian order all books on the "sacred art" to be destroyed lest the Egyptians should become rich enough to throw off the Roman yoke? The books which survived this decree, such as those recently found at Thebes, contain nothing but rambling and very rough indications regarding various alloys. The twenty-eight books which Zosimus is supposed to have written on the subject are, unfortunately, lost.

It was not till the seventh century of our era that Egypt again became the focus of the art to which it had given birth. For after the Serapeum at Alexandria was destroyed, Greek learning had fled to Constantinople. It was the Arabs who raised again the torch of learning which their own military exploits had done so much to extinguish. It is they who became the depositaries of the arts until the eleventh or twelfth century, and Abu Mansur's *Principles of Pharmacology,* a work written in Persian, is the chief compendium of chemical knowledge of that period.

Then came Albertus Magnus, the retired Bishop of Regensburg, a noted alchemist. Thomas Aquinas, the founder of scholasticism, was firmly convinced of the truth of alchemy, and Roger Bacon, the English Doctor Mirabilis of the thirteenth century, wrote an elaborate treatise which he called *The Mirror of Alchemy.* Villanova, too, boasted that he would "tint the sea if it were mercury," meaning that he could convert any amount of mercury into gold. Raymond Lully put forward the principle that all metals consist of mercury and sulphur in various proportions, and this idea led to the long series of attempts, initiated by Geber or Djabar, to "fix the mercury." Alchemy found a powerful protector in England in the person of Henry VI, who wanted money for war purposes, and whose "Rose nobles" played havoc with the credit of the English coinage.

The work of the alchemists was not entirely fruitless.

Several new metals and compounds were discovered. The balance came to be used in cupellation and cementation processes, and had not the line of inquiry been diverted into medical channels, Lavoisier's quantitative analysis might have been anticipated by three centuries. Zinc was discovered. It was thought to be an inferior kind of silver, and its oxide was worked up into salves. Bismuth also became known, and Basil Valentine, a German alchemist, published a really creditable work on antimony and its compounds, under the sounding title, *The Triumphal Car of Antimony.*

The idea of transmutation is found more among the European alchemists than among the Orientals. A passage attributed to Geber runs as follows: "To assert that one substance can be produced from another which does not contain it is folly. Since, however, all metals consist of sulphur and mercury, we can add to them the constituent in which they are deficient, or abstract the one which is present in excess. In order to achieve this, make use of the arts: calcination, sublimation, decantation, solution, distillation, coagulation (crystallisation), and fixation. The active agents are the salts, alums, vitriols, borax, the strongest vinegar, and fire."

It is noteworthy that the above passage does not enumerate the mineral acids, for in other works attributed to Geber we find mention of sulphuric acid and nitric acid (*aqua fortis*), and *aqua regia* is described as the long-sought alkahest or universal solvent, capable of dissolving even gold, the "king of metals," and converting it into "potable gold," a medicine of marvellous efficacy.

With the advent of Paracelsus and the iatro-chemists alchemy gradually drifted into the fantastic absurdities which found their last refuge among the Rosicrucians and Illuminates, and their last notable champion in the Dutch chemist Boerhaave. The "sacred art" became more involved and obscure as its success became more doubtful. The search for the Philosopher's Stone, the Grand Elixir, the Master-Piece, the Fifth Essence, which was to convert all metals into gold and prolong life indefinitely, was wrapped up in mystic allusions to dragons, red and green lions, white swans, queens, and lilies, and the planets were invoked when all earthly powers failed.

And then came the portent of Paracelsus. He came like a whirlwind, and shook the "sacred art" to its very foundations. "The object of chemistry," he exclaimed, "is not to make gold, but to prepare medicines." While holding the chair of Medical Science at Basle, to which he was appointed in 1525, he waged incessant war on the orthodox physicians of the school of Galen and Avicenna, proclaiming that the human body, of the earth earthy, consisted of mercury, sulphur, and salt, which latter had been added to the primary constituents of metals by Hollandus in the previous century. Of these, mercury represented volatility, sulphur oiliness or combustibility, and salt firmness. All diseases were caused by excesses or defects of one of these constituents, fever and the plague being due to an excess of sulphur, paralysis and depression to mercury, and so on. The remedy was to restore the balance by taking the proper chemicals. Hence the drug and "bottle" system, which is dying a hard and belated death in our own days. Copper vitriol, corrosive sublimate, sugar of lead, the "infernal stone" (silver nitrate), and various antimony preparations were among the heroic remedies advocated and boldly employed by that redoubtable "kill-or-cure" practitioner. His professorship lasted for two years only, but his fame endures to this day, having lost but little of the glamour which surrounds commanding personalities of striking originality.

His Flemish successor, Van Helmont, was the first to pronounce in clear language that an element is something indestructible, which persists without change of properties throughout the series of combinations which it may be made to enter. He discovered, in fact, the fundamental law of chemistry, the law of the conservation of matter, without, however, putting that law to its proper use in quantitative analysis. Beside the law, he also gave us a word. He deliberately coined the word "gas" instead of the word "air," which had, up to his time, been indiscriminately applied to all gases. He admits himself that he thought of the word "chaos" when he enriched all the world's languages with a new and necessary term. He applied the term, in the first instance, to carbon dioxide, the "fixed air" found in brewers' vats, and absorbed by limewater.

The medico-chemists were mostly alchemists at heart. Sylvius, who identified respiration and combustion, was an alchemist, and so were many men who, like Agricola, Palissy, and Glauber, advanced metallurgy, ceramics, and chemical industry by valuable discoveries. Tachenius alone, who first discovered that salts are combinations of alkalies and acids, criticised and ridiculed the aims and claims of the gold-makers.

We must not judge these early chemists too harshly. In those days no encouragement was given to pure science. In fact, it was quite the opposite. Open and fearless thinking was considered dangerous to established authority and vested interests. In the Græco-Roman days, and again among the Arabs, the prevailing systems of slavery cut off the educated few from manual occupations and from opportunities of getting into touch with nature. Mediæval serfdom had a similar effect. The towns alone, and sometimes the courts of princes, held out inducements to scientific achievement. But even then the utility had to be obvious and unquestioned. First, it was the making of gold, the acquisition of enormous wealth at a trifling cost. Then it was the curing of bodies and the prolongation of life. None could gainsay the value of such discoveries, could they but be made; and so we find effort concentrated into those main channels. We cannot doubt that the magic and mystery of matter had some attraction too. The rocks and stones from which all tangible things could be made held out a perpetual allurement to the inquiring mind. Had that mind been free from the incubus of authority, from prejudice and preconceived opinion, the "call of the wild" might have proved irresistible even then. But there was Plato and Aristotle; there was the elaborate syllogistic system of scholasticism, prepared to crush and devour all virgin thought in its all-powerful jaws. Everything was prejudged, prevalued, and pre-empted. It is not that the modern candid inquirer is free from the thraldom of authority. But that authority is now democratic, flexible, and admittedly and deliberately fallible. No superhuman sanction is claimed for it. There is not a law of chemistry which is not open to criticism and attack, and when a fundamental law—let us say the indivisibility of the atom—is attacked and disproved, there is not a shout of execration, but a chorus of jubilant congratulation. Moreover, our leaders nowadays do not attempt to gloss over the weak points in their generalisations. They emphasise them, and point them out to the rank and file, so that those who press on behind them may know where to look for new laurels.

It was the seventeenth century which saw the first lull in the national, economic, and religious struggles of Europe. The latter half of it saw the first steps towards the organisation of scientific research. The Royal Society, which grew out of Boyle's "Invisible College," began to publish its Transactions in 1665. The following year saw the foundation of the Académie Royale at Paris. Berlin, St. Petersburg, and Stockholm followed with similar institutions. The keynote of the new chemistry was struck by Boyle, who was President of the Royal Society in 1680. He considered, he said, the art of chemistry "not as a physician or alchemist, but as a philosopher." Elements, he said, were such bodies as could not be decomposed by chemical means. He attempted to found a "corpuscular philosophy," and even attributed heat to the violent motion of the particles of bodies, but failed to apply this brilliant guess to the "spring of the air," which he himself investigated with such painstaking and successful ingenuity. It was he, also, who first used the word "analysis."

And so we come to the eighteenth century, the age of "phlogiston," or flame-substance, another wonderful coinage due to Van Helmont. It was Stahl, physician to the King of Prussia, who erected the doctrine of phlogiston into a system. He took up Becher's theory, which made all inorganic substances consist of three earths in various proportions—viz. a mercurial, a vitreous, and a fat or combustible earth. This last was identified by Stahl with the element phlogiston, which escaped on burning. Substances which, like carbon, left little residue, and did not distil or sublimate, were taken to consist of nearly pure phlogiston. When a metal was burnt, the resulting oxide was supposed to be the earthy residue or "calx" of the metal left after the phlogiston had escaped. That the oxide was often found to be heavier than the original metal was attributed by Boyle and others to its having taken up some "fire-stuff" from the air—a view which, when properly interpreted, is quite in harmony with modern notions. The last and most distinguished of the German phlogistonists was Marggraf, who first distinguished alum from magnesia, and found cane-sugar in the red beet. It was he, also, who first applied the microscope to chemical problems. He found himself that phosphorus increases in weight by combustion, but even that did not cure him of his phlogistic prejudice, and he retained it to the end of his life.

Meanwhile, the same doctrine was developed in France by Geoffroy, who compiled the first Tables of Affinity; by

Duhamel, who prepared pure soda, and proposed to manufacture it from rock-salt; by Rouelle, who distinguished between acid, basic, and neutral salts; and by Macquer, who successfully applied chemical discoveries to pottery and dyeing.

In Great Britain there was the great Joseph Black, renowned as much in physics as in chemistry, who discovered latent heat in 1762, and carried out some splendid researches on carbonic acid and the carbonates. He showed how the latter become caustic on being calcined, owing to the "fixed air," CO_2 (Van Helmont's *gas sylvestre*), being expelled. Henry Cavendish, that rich recluse who loved to keep his discoveries to himself, thought he had found the real phlogiston when he discovered hydrogen. That a man who could analyse water into hydrogen and another gas, describe air correctly as the mixture of two gases, and even forecast the discovery of argon, should be a consistent upholder of a doctrine which his own discoveries did most to subvert, must astonish and also reassure us. For it shows, if nothing else, that none of our accepted laws, however firmly upheld by the highest authorities, are quite safe from demolition.

With Priestley in England and Scheele in Sweden, the two independent discoverers of oxygen, we reach the last of the great names in the phlogistic roll. Scheele (who, on a memorable occasion in his laborious life, exclaimed: "It is the truth alone that we desire to know, and what joy there is in discovering it!") found four new substances in rapid succession—chlorine, oxygen, manganese, and baryta, and first observed the successive stages of oxidisation in iron, copper, and mercury.

The phlogistic doctrine was now tottering to its fall. The man who knocked it down was Lavoisier, a well-educated Frenchman, who, as farmer-general under the old regime, was in charge of the Government saltpetre works, and had ample opportunities for research. In his hands, the balance became what it is now, the chief instrument of chemical investigation, the ultimate arbitrator in matters of chemical theory. When he heard of Priestley's discovery of oxygen in 1774, he guessed at once that the new gas must be the substance which combines with Cavendish's "inflammable air" to produce water. He now held the key to the whole question of combustion. He turned phlogistic discoveries into weapons for the demolition of phlogiston. He burned a diamond, and proved that it produced carbonic acid, combining with the oxygen of the air in the process. He weighed tin before and after calcination, and identified the difference of weight as the weight of oxygen required for oxidation. Finally, he explained the evolution of hydrogen on dissolving metals in acids.

It was this last assault which took the phlogistic position by storm. When zinc dissolves in an acid and becomes a calx or earth, it loses its phlogiston, which escapes in bubbles. So said the phlogistonists. It seemed the only way to account for the bubbles, especially as no loss of weight could be found in the water. But Lavoisier now showed that the bubbles were hydrogen liberated by the decomposition of the water, the oxygen going to form the oxide and the hydrogen escaping.

That happened in 1783. It was the birth of Modern Chemistry. The rest of Lavoisier's life, which ended on the guillotine during the Reign of Terror in 1793, was spent in propagating the new doctrines and confounding their enemies. He used equations to denote chemical reactions, and established the nomenclature which, in its main features, persists to the present day. His immediate successors in France—Fourcroy, Morveau, and Berthollet—founded the "Annales de Chimie," and proudly styled the remodelled science "La Chimie Française." Of these three Berthollet appeared as the champion of Variable Proportions against Proust of Madrid, who fought for Constant Proportions, in the famous controversy which raged from 1799 to 1807, and was eventually decided in favour of Proust. It must be remembered, however, that Berthollet was not altogether in the wrong. The doctrine for which he fought has since been revived as the Law of Mass Action.

It is strange to think that all this great and fruitful work was done without the Atomic Theory. The "atoms" of Democritus, the "corpuscles" of Boyle, had remained barren of all results for chemistry. It remained for the colour-blind Dalton of Manchester to expound, in his *New System of Chemical Philosophy*, published in 1808, a doctrine which is now the very foundation of chemistry—a doctrine without which present-day chemistry can hardly be conceived. The "constant proportions" for which Proust had fought so successfully were now given an interpretation of wonderful simplicity. A certain quantity of oxygen was always required to convert zinc completely into its oxide, simply because both zinc and oxygen consisted of numberless corpuscles, equal among themselves and indivisible, and zinc oxide consisted of an assemblage of pairs of these atoms, one atom of oxygen to each atom of zinc. The idea of absolutely identical atoms for a given substance does not seem to have presented much difficulty at the time. It was more difficult to conceive how each atom of copper or mercury could sometimes be satisfied with half an atom of oxygen, a contradiction in terms!

So long as relative combining weights were the only criteria of atomic weights, the atomic theory could hardly hope to survive a searching criticism. But when Dulong and Petit, in 1819, discovered their law of Atomic Heat, and Mitscherlich discovered Isomorphism, two additional guides to the weight of the atom became available, and these were followed up by the criteria of Vapour Density (Dumas, 1827) and Electrolysis (Faraday, 1834). The atom was thus rediscovered along five independent lines, seen, so to speak, from five different points of view.

At the same time, the conceptions of electrolysis, assiduously cultivated by Davy and Berzelius, threatened (as they do again in our days) to overrun the entire field of chemistry. To the great Swede, every atom or combination of atoms was naturally and inevitably either electro-positive or electro-negative. This was a dualistic system, and the division was as profound and permanent as the division of the sexes. It was only abandoned in 1825, when it was proved that hydrochloric acid contains no oxygen. The great German chemist, Liebig, who "thought in phenomena," and made the first meat extract, propounded in 1834 a new view of acids, in which not oxygen, but hydrogen, played the essential part. Simultaneously, his great colleague Wöhler broke down the outer defences of "vitality" by manufacturing urea out of inorganic material. Henceforth, organic chemistry took the lead, and Dumas's Type Theory became the inspiring principle of research. "There are in organic chemistry certain types which remain unchanged, even when their hydrogen is replaced by an equal volume of chlorine, bromine, or iodine." Thus, the type theory according to Dumas. Laurent, Hofmann, and Williamson extended the theory till the water type was made to include both alcohol and ether. Gerhardt amalgamated it with the older Radical theory, distinguishing between water, hydrochloric acid, ammonia, and hydrogen types; but in his hands the system tended to degenerate into a somewhat empty formalism. "Give us facts alone!" cried Gmelin (somewhat unscientifically), and Kolbe and Frankland were soon busy making "history" by converting alkyl cyanides into fatty acids and performing sundry other feats unheard-of. It was Sir Edward Frankland who, in 1852, put forward the law of Saturation Capacity, or Valency, and supported it by his brilliant researches on the compounds of metals with organic substances. And when the Sicilian reformer and patriot, Cannizzaro, revived the principle of Avogadro in 1858, chemistry was endowed with its two most powerful modern weapons. Valency gave us our modern Structural Formula. The principle of Avogadro defined for us the molecule as distinct from the atom, and rescued the atomic theory from the gulf into which it had fallen in the confusion between the ultimate units of physics and chemistry respectively. In the same year, 1858, Kekulé, of Bonn, discovered the fourfold valency of carbon, but announced it in a manner only half serious—a strange début for a principle which, as Ernst von Meyer says, "now illumines the whole field of chemistry."

Couper, Butlerov, and Erlenmeyer were soon busy evolving structural formulæ and links, or "affinity-points." Kekulé gave us the Benzene Nucleus, and, incidentally, the vast and aromatic industry based upon coal-tar. Van't Hoff and Lebel laid the first foundation of Stereochemistry, while Kopp founded Physical Chemistry, and the great Siberian Mendèleeff discovered the key to the evolution of the elements in his famous Periodic System.

And so we arrive within touch of the living, breathing chemistry of to-day—a science which commands a vast army of workers, which publishes annually some five thousand researches, and which, in its ultimate issues, largely controls the economic fate of nations.

CHAPTER III

THE MOLECULE

TWO years ago I ventured to predict that molecules would soon be studied microscopically. This has since been accomplished by means of Brownian motions and the ultra-microscope. De Broglie succeeded in photographing particles of tobacco-smoke—whose blue colour indicates their excessive minuteness—by concentrating upon them the light of an arc-lamp, and giving an exposure of three seconds with a magnification of forty diameters.* It is true that these particles have a diameter (5×10^{-6}cm.) which is 250 times that of the hydrogen molecule; but then the hydrogen molecule is the smallest molecule known, except that of helium, and many molecules of complex organic substances have the diameter of these tobacco particles, which may, indeed, be molecules themselves. In any case, De Broglie was capable of observing much smaller particles than these, but could not photograph them on account of their speed. By diffusion experiments he found that their diameter was of the order of 10^{-7}cm., which is only about four times as large as the molecule of ethyl chloride.

We are face to face, then, with this extraordinary situation: the molecule has ceased to be a theoretical abstraction—it has become a visible and tangible reality; for we can not only see it, but also "manipulate" it—not, indeed, with our hands, but by means of heat and electricity and the air-pump. We can accelerate or retard its motion by regulating the temperature; we can increase or reduce its free path by regulating the pressure; we can even, by means of radium rays, make it take up one or two electrons, and thus force it, by means of a suitable electrostatic field, to go whithersoever we please.*

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* See *Comptes Rendus*, 148, pp. 1163–4, May 3, 1909.

This remarkable advance opens an entirely new chapter in chemistry. Ramsay's "tenth of a milligramme" is no longer the utmost limit of manipulation. Pure chemistry has once more become indebted to physical (in this case, optical) methods for an immense extension of its powers. Since the advent of Arrhenius and Van't Hoff we have been accustomed to look upon the dilute solution as the best known and most thoroughly investigated material structure. Now that distinction will have to be conceded to the gases. Chemical history seems to work in a circle. After chemists had been for centuries dealing almost exclusively with liquids, solutions, and concoctions innumerable, Dalton, Gay-Lussac, Avogadro, and Davy erected their "pneumatic philosophy" into a new system of chemistry based upon the conception of atoms and the observed volumes of combining gases; and now, after so many years spent on the properties of dissolved and dissociated molecules, the work of half a dozen French experimenters is forcing back our attention to the gaseous state, just as their engineers are conquering the air.

In chemistry, as in aërial navigation, theoretical difficulties have a way of disappearing before a sufficiently determined onslaught. We used to be told that molecules would never be seen—first, because they are so much smaller than the shortest visible light-waves, and, secondly, because their vibratory motion would be so rapid as to make them inappreciable to the eye. But although we do not see molecules as they are, yet we see something which tells us of their whereabouts, just as a fixed star—theoretically a mere geometrical point, without perceptible dimensions—indicates its place to us by the diffraction-disc formed on the focal plane; and the vibration of the molecules happens to be rendered innocuous by that curious "persistence of velocity" which keeps the molecules moving in approximately a straight line, in a series of invisibly small jerks, thereby producing an actual impression of a much slower and steadier motion.

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* **De Broglie and Brizard, *Comptes Rendus*, p. 1316, May 17, 1909.**

The discovery of the molecule, like that of Neptune, is one of those achievements which serve to bring out the extreme utility of a comprehensive theory. When Dalton put forward his atomic theory he had no idea of the actual number of atoms present in a given volume of gas; and Avogadro, when he announced his famous principle, was equally in the dark. Their vision was symbolic. Ours has now become actual. The kinetic theory of gases thus enters upon a new era. When Leucippus first put forward the idea that all visible things consist of aggregations of hard, indivisible, and similar parts, he was probably performing a piece of idle speculation such as the ancients were fond of indulging in. Gassendi—who, in the seventeenth century, followed along the lines of Leucippus, Democritus, and Epicurus—elaborated an atomic theory in which the indivisible particles were pictured as similar in substance, but different in size and form, and moving rapidly in all directions through empty space. Gassendi gave substantially the modern theory of the three states of aggregation. In 1738, Daniel Bernoulli published his *Hydrodynamica*, in which he, for the first time, guessed that the pressure of a gas may be due to the impact of its molecules on the boundary. He showed how Boyle's law could be accounted for, and even began to take into account the finite size of the molecules—then, of course, quite undetermined.

This step was not followed up for nearly a hundred years; but between 1821 and 1857 we have Herapath, Waterston, Joule, Krönig, and Clausius working out the mathematical theory, the last-mentioned succeeding in calculating the ratio of the two specific heats for a monatomic gas. Then in 1859 came Clerk Maxwell's first attempt to get within hailing distance of the molecules—to get some rough idea of their size and number. He was stimulated in this endeavour by his success in dealing with the stability of Saturn's rings. He showed that these must necessarily consist of discrete particles, and was awarded the Adams Prize for this work in 1857. Maxwell deduced the "mean free path" of a gaseous molecule from observations on the viscosity of gases, and, independently, from the rate of diffusion of olefiant gas in air. It is obvious that if the molecules were geometrical points their paths would never cross each other. There can be practically no encounters in a chaos of geometrical points. If, therefore, there is any evidence of encounters between molecules, it is an encouraging sign that we need not despair of arriving at some idea of their dimensions. The matter may be clinched in this way. Granted that gases consist of molecules moving at a high average speed, then, if there are no encounters between molecules, any gas entering another should diffuse instantaneously throughout the other. In fact, if we turn on the tap of our illuminating gas, the smell should be perceived at nearly the same instant in every part of the room. This is far from being the case.

But it yet remains to be proved that molecules do move with great speed. A rough idea of this speed may be obtained in a very simple manner. Granting that the pressure of a gas is due to the impact of its molecules, we need only calculate what average speed would be necessary to make a given weight of gas exert a certain pressure. This problem would present no difficulty in the case of, say, a jet of water directed against a door kept open by a spring. Knowing the size of the jet, we could easily calculate what speed would suffice to exert a certain force upon the door—and we should not have to trouble about the molecular constitution of the water. In the case of a cubic centimetre of air (which weighs 0·00124 grm. at 15 deg. C.) we could easily calculate what average speed would endow it with a pressure of one atmosphere; but we should have to remember that only one-sixth of the total impinging molecules are, during any given period, impinging on one side of the centimetre cube.

A still simpler way is to equate, with Maxwell, the pressure per unit area with the energy per unit volume. In the case of one atmosphere the pressure is approximately a million dynes per sq. cm. (more correctly, 1,013,600 dynes). This pressure must be equal to the kinetic energy $\frac{1}{2}mv^2$ of the air contained in the cub. cm. It weighs 0·00124 gr., and its kinetic energy is, therefore,

$$\frac{v^2}{2} \times 0{\cdot}00124 = 10^6,$$

which gives $v^2 = 16 \times 10^8$. This, then, is the mean square of the molecular velocities. The square root of this is 40,000 cm. per sec., or about 900 miles per hour. This prodigious figure was known already to Clausius. It means that the gas from the tap should take not more than one-fiftieth of a second to pervade a good-sized room uniformly.

The question was at this stage when Maxwell took it up. He had sufficient genius to seize his opportunity. He attacked the problem along two independent lines. He allowed olefiant gas to escape into the air and measured its rate of diffusion. He also measured the amount by which a jet of gas is retarded by the immobility of the surrounding gas. This retardation is the result of an interchange of speeds between the moving jet and the stationary gas, due to collisions between molecules of each penetrating into the other. The more frequent such collisions are, the greater is the retardation. The amount of retardation, therefore, gives an indication of the number of collisions per second—or, in other words, the average length of the free path of each molecule between one collision and the next. The result was of the order of 10^{-5} cm., so that in a cubic centimetre each molecule would have to describe its path from wall to wall in no less than 100,000 jerks at the least.

Once the mean free path is known, it becomes comparatively easy to calculate the number of molecules which produce these collisions—i.e., the number of obstacles which, moving with a certain average velocity, would suffice to stop another molecule, moving with the same average velocity, so many times per second. This was first done by Johnstone Stoney in 1860—immediately after Maxwell's calculation appeared. Boltzmann, Kirchhoff, van der Waals, Tait, Lorentz, Lord Rayleigh, Burbury, and Jeans have since followed with further investigations. The value now generally accepted is 4×10^{19} (40 trillion) molecules per cub. cm. at standard temperature and pressure. Thus, then, we have reduced Avogadro's principle to a definite figure. According to Avogadro, every unit volume of gas of any kind contains, when at standard temperature and pressure, the same number of molecules. That number, as we now know, is 40 trillion per c.c.

Now, what does that principle actually imply? Its main import is to teach us something about the nature of temperature. We recognise pressure as due to the translational energy of a very large number of small particles. It is divisible into two factors— viz., the number of particles per unit volume, and their mean translational energy. The second factor is the temperature. If the particles of two gases have different weights, then, if the temperatures are to be equal, the average square of speed must vary inversely as the molecular weight. This is, in fact, Graham's law of diffusion. This law has recently received a considerable extension. It can, with equal justice, be applied to electrons. They are between 1000 and 2000 times lighter than hydrogen atoms, or, say, 3200 times lighter than hydrogen molecules. Hence their speed will have to be fifty-six times that of hydrogen molecules, and 224 times the speed of oxygen molecules, at the same temperature. This gives us speeds of 10^7 cm. per second, even at ordinary temperatures, and when the temperature rises to a red or white heat we can well imagine electrons rushing out freely from the surface of a metal, as has been actually observed—notably when covered with a layer of calcium oxide.

But the significance of the molecular discussion of temperature is much deeper than this. In most gases, the work spent on increasing the temperature of a gas does not tally with the actual increase in kinetic energy. In oxygen, only about three-fifths of the work spent is recovered in that way. In mercury vapour and in Ramsay's "noble" gases, Argon, Krypton, Xenon, and in helium, the entire work is recovered in the rise of temperature. The obvious conclusion is that the energy supplied to the other gases is frittered away on things for which it was not intended. It cannot, of course, disappear, and so it follows that there must be some "internal" forms of energy which are increased by the amount reported missing. And here, again, we come into hand-grips with the internal arrangements of the molecule. Those molecules which hide away their energy have more "degrees of freedom" than those which do not. This conception of degrees of freedom is becoming an important one in molecular chemistry, and we may therefore illustrate it by some examples. A geometrical point which is free to move along a given line has only one degree of freedom. If it is confined to a given plane, it has two degrees of freedom. If it is free of space, it has three degrees. If instead of a point we have a sphere, that sphere can not only move as a whole with all the freedom of a point, but can also revolve independently about three axes at right angles to each other, and about two or three axes simultaneously. It has, therefore, six degrees of freedom. If we fix its centre at a certain point, it has only three.

Now, we have learnt, since Boltzmann, that the energy of a molecule in what is called a "conservative" system (which cannot exchange energy with bodies or space outside) is equally distributed over its several degrees of freedom. Those which consist of rotations do not appear to us as heat. They are hidden or latent. Not only that, but we know how to calculate the degrees of freedom possessed by a gas by the formula—

$$C_p/C_v = 1 + \frac{2}{n+3} = \gamma,$$

where C_p is the specific heat of the gas at constant pressure, C_v the specific heat at constant volume, and n the number of degrees of freedom beyond those of pure translation. When $n=0$ the energy is all translational, and the expression becomes $1+{}^2/_3$, or 1·67, which is the ratio actually found for mercury vapour and the "noble gases." These are all "monatomic" gases—i.e., gases in which the molecules consist of single atoms. These atoms, as far as temperature is concerned, behave like geometrical points. But, on the other hand, we know from viscosity experiments that they have a diameter only slightly below that of hydrogen molecules.

What, then, must we conclude from this? The atoms collide, but do not make each other rotate. This would be the case if they were perfectly smooth spheres, and this is usually assumed to be true. Still, we must not be too hasty.

All we *do* know is that a helium atom, hitting upon another at any angle, wastes no energy in making it revolve about itself. That is the root fact. The interpretation is yet to seek. We do not yet actually know what a "collision" really means. It may, for aught we know, be something like the entry of a comet into our Solar System, and its approach to and recession from the sun along a hyperbolic orbit. Both the sun and the comet escape without a perceptible rotation being imparted to them.

Now, what happens when the molecule is not a sphere? If it is a spheroid like the earth, an impact along the equator will, as before, produce no rotation. But an impact along a meridian will, and this impact may produce a rotation about two equatorial diameters at right angles to each other. Hence, we have two new degrees of freedom capable of absorbing energy, and $n=2$. If there is no axis of symmetry, $n=3$.

It is curious and significant that we cannot have $n=1$, and this is corroborated by the actual behaviour of gases, as will be seen from the following table:—

	n	γ
Mercury vapour	0	1·67
Krypton	0	1·67
Helium	0	1·67
Argon	0	1·67
Hydrogen	2	1·4
Nitrogen	2	1·4
Carbon monoxide	2	1·4
Nitric oxide	2	1·4
Oxygen	2	1·4
Hydrochloric acid	2	1·4
Chlorine	3	1·33
Carbon dioxide	3	1·33
Nitrous oxide	3	1·33
Ethylene	5	1·25
Methylene chloride	6	1·22
Chloroform	10	1·154
Carbon tetrachloride	12	1·13

Attempts have been made by Naumann, Thomson, Capstick, Strecker, and others to establish a relation between *n* and the number of atoms in the molecule, but so far with little success. It appears that a halogen atom can be substituted for a hydrogen atom without making much difference to *n*, but a second substitution makes a great difference. This was especially found by Capstick in chlorinating the paraffins.

Here, then, we have another physical method which brings us into direct touch with the shape of the molecule. We may conclude, at all events, that a binary molecule like H_2 or O_2 is symmetrical about two axes at right angles to each other, just as we might expect it to be if it were formed by the conjunction of two spherical atoms.

Further attempts to draw conclusions from the internal degrees of freedom of molecules are complicated by the fact that a gas is not in reality a "conservative system." All gases, as we know, radiate and absorb heat. They do so slightly, but quite perceptibly. The sun's rays warm the air above us. Now, this means, according to modern notions, that the molecules contain electrons capable of vibrating or revolving in definite periods. Either that, or that they contain free electrons. We can distinguish the two cases of absorption by noting whether the absorption spectrum of the gas consists of lines or bands. The spectra of the gases formerly called "permanent," are line spectra, while water-vapour and most carbon compounds show band spectra, some of which may, however, be series of lines incapable of analysis.

Now each of the spectrum lines indicates a separate degree of freedom in the molecule of the gas concerned, or rather, perhaps, in the various molecules of the gas in turn. These degrees of freedom do not, however, affect the quantity γ. And here we enter a most promising field of investigation. How many atoms in an incandescent gas are at any given instant actually emitting spectrum lines? How many lines does each atom emit? Is this emission affected by the position of the atom in the molecule? Does the emission of a complicated series of lines indicate a complicated spectrum of every molecule, or does it indicate a rapidly succeeding phantasmagoria of changes? Do the "main series" and "subsidiary series" of spectrum lines belong to identical atoms, or do they belong to rapidly alternating allotropic forms of the substance?

These fascinating questions might be multiplied. In spite of the work of Ritz, and other pioneers, we are still some distance off a plausible theory of spectra. If we could only combine the new method of Brownian motions with the spectroscope, some very striking results might be obtained. It is a matter of the most intimate structure of the atom.

CHAPTER IV

STATES OF AGGREGATION

"NATURE does not make a jump." That old Latin proverb has received several new illustrations in the course of modern chemical research. Liquid crystals and solid solutions have broken down the boundary which formerly separated the solid and liquid states of aggregation, and at the "critical point" a liquid can barely be distinguished from its vapour.

When Crookes discovered the remarkable behaviour of cathode rays in a high vacuum, he thought he was face to face with a fourth state of matter. This "radiant" matter, he pointed out, had lost all its chemical characteristics, and this was but the climax of a process whereby the distinguishing properties of bodies were gradually reduced in number by taking them from the solid up to the gaseous states.

We do not look upon cathode rays nowadays in that light, but the remark regarding successive states of aggregation still holds good. The gaseous state does not offer such variety as either the liquid or the solid states. It is only when the molecules come into intimate contact that they realise each other's boundless possibilities. In the rush and turmoil of the gaseous state distinctions are obliterated, even as they are in a bustling crowd of men. That a single substance may show quite a number of distinct phases in the liquid state alone is strikingly shown by that remarkable body, cholesteryl cinnamate, recently (1906) discovered by Frans Jaeger, of Amsterdam. At ordinary temperatures it is a brown solid, but at 151° C. it softens, and exhibits a brilliant display of colours, until at 157° C. it is a thick orange-red liquid, which, unlike ordinary liquids, shows double refraction, and thus proves that it has a crystalline structure. If this is stirred, the liquid crystals are seen to form links of lustrous plates, some of them violet, and other bright green. On raising the temperature further the liquid becomes thinner, and nearly colourless. But at a temperature of 199·5° C., another change supervenes. The liquid becomes suddenly thicker, and assumes an enamel-white appearance, eventually separating into two layers, both of which show traces of a crystalline structure. Two degrees beyond that the scene shifts again, and we obtain a clear, colourless liquid from which all crystalline character has disappeared.

In this case the transition from the solid to the liquid state is spread over 50 degrees. It is an unusually long agony. But it makes it possible for several unstable liquid phases to exist for a short spell. If the melting of tin or lead were as gradual, we might find as many intermediate steps. In solids we are already familiar with a number of allotropic states which are stable under various conditions of temperature and pressure. Ammonium nitrate is known in four different crystalline states, and thallium nitrate in three. The varieties of sulphur and phosphorus, and the allotropic state of tin which is stable in extreme cold, and gives rise to the "tin plague" in cold climates, are familiar instances. Even in ice, which we are accustomed to regard as a simple standard substance, Tammann distinguishes three distinct varieties, with different critical constants. The whole tendency is to find variety where we formerly saw uniformity, to break down boundaries, to obliterate distinguishing landmarks, and to set up new and more generalised distinctions in their place.

CONSTITUENTS, COMPONENTS, AND PHASES

Modern attempts to reduce the chaos of solids, solutions, and vapours to some kind of order have given rise to a number of new terms and conceptions. The old terms mixture, compound, constituent, no longer suffice. We must carefully distinguish between substances which may be arbitrarily varied in their relative proportions, and those which cannot. The latter are termed "constituents." Water has two such constituents, viz. hydrogen and oxygen. Common salt has two, viz. sodium and chlorine. But in a solution of salt in water the proportion of salt may be varied within wide limits, from an infinitesimal amount to one-third the weight of the water which holds it in solution. Water and salt are the "components" of the solution. The fact that in highly dilute solutions most of the salt is dissociated into Na and Cl ions does not add a new component to the number present. For neither the dissociated salt nor the relative proportions of the ions are independently variable. We could, however, obtain a new component by adding either chlorine or sodium in excess. Such a component would not be a "constituent" of anything. It is clear, therefore, that we may have constituents which are not components, and also components which are not constituents.

Another important point in the definition of the "component" of a system of chemical substances in mutual equilibrium is that the component must take part in that equilibrium. Its presence must be essential to equilibrium, must be a determining factor in it. Thus, the presence of sand in a salt solution does not sensibly affect the equilibrium, and sand is not a component. We now require a precise definition of the word "phase." It is sometimes rather loosely employed; but if we remember that all phases are separated in space, and have, in fact, definite bounding surfaces, the conception becomes clearer. In water we distinguish the solid, liquid, and gaseous phases. A solid may consist of a conglomerate of various crystals, and then it contains as many phases as it has types of crystals. Even when these are microscopic, we must still uphold that distinction. Thus, solid iron consists of a number of phases, which we have learnt to distinguish as ferrite, cementite, perlite, etc. A liquid, also, may contain several phases, in so far as it consists of several layers of different composition or concentration. There must, however, be a definite boundary. A gradual transition does not suffice, or we should have to admit an infinite number of phases in a cup of tea.

VARIABILITY

What gives a practical interest to these new conceptions is that the various phases and components of a "system" of chemical substances limit each other's freedom in a manner capable of a simple formulation. Taking any single phase by itself, we may change its temperature and pressure within pretty wide limits, without converting it into another phase. We can, at all events, alter both the pressure and the temperature. Ice, water, and steam may each be obtained under various pressures, and at various temperatures. But as soon as we have two phases together we can only alter either the pressure or the temperature. If we attempt to change them both arbitrarily, the two phases immediately reduce themselves to one. This curious fact may be illustrated by some familiar examples. Boiling water at 100° C. gives off steam, exerting a pressure of one atmosphere. If enclosed in a tube and surmounted by a piston, the piston will be forced up against the pressure of the air as soon as the water boils, but not before. At 120° C. an extra atmosphere of pressure will be necessary to hold the piston down, but the slightest reduction of the temperature, unaccompanied by a corresponding reduction in pressure, will immediately condense the vapour, and give us one phase instead of two. And, conversely, if we maintain the pressure below two atmospheres, and raise the temperature a few degrees above 120°, the whole of the water will become vaporised, and we shall again have only one phase.

In a mixture of water and ice a similar state of things exists. Only the pressure required to alter the melting-point by a few degrees counts in hundreds of atmospheres. Even in a mixture of ice and water-vapour, there is a definite relation between pressure and temperature. Ice may, in fact, be completely vaporised without fusion by simply keeping it in a vacuum not exceeding 4 mm. of mercury, enlarging the vessel as evaporation proceeds and the vapour accumulates.

A single phase has, therefore, two independent variabilities. Two phases together have only one. The former are called "bivariant" systems, the latter "univariant" systems. When we take all those phases together, all power of variation is lost, and we obtain an "invariant" system. Such an invariant system is ice, water, and steam. It has a fixed temperature, viz. 0·0076° C. (practically freezing-point), and a fixed pressure—viz. 4·6 mm. of mercury. The slightest increase of temperature eliminates the ice; the slightest increase of pressure eliminates the vapour. Decrease of pressure gradually evaporates all the water and ice; and decrease of temperature solidifies all the water and vapour. That this must be so is evident on a short consideration. A system of water and steam can be reduced in temperature and pressure, a definite pressure corresponding to each temperature. This reduction can go on until the water freezes. While it is freezing, the temperature is stationary. It remains stationary until the water is frozen, i.e. until the liquid phase has disappeared. If, therefore, the liquid phase is to be retained, the temperature must stop short of the freezing-point. As the pressure has been supposed constant, the system will be "invariant."

THE PHASE RULE

A remarkable relation between phases, components, and variabilities was discovered in 1877 by Willard Gibbs, of Yale. It is called the Phase Rule, and may be written as follows:

$$F = C + 2 - P.$$

Where F is the number of variabilities or "freedoms," C is the number of components, and P is the number of phases of a system in equilibrium.

Before going any further, we may verify this rule in the case of water. Ice, water, steam are three phases of one component, viz. H_2O. Hence, we have $P = 3$, $C = 1$, and $F = C + 2 - P = O$. In other words, the variability is zero. The system in which all the phases are present is invariant. If there are only two phases, say, water and steam, $F = 1$; the system is univariant. Water by itself is bivariant. If there are as many phases as there are components, $C = P$, and $F = 2$. Thus, if there are any number of liquids in layers one above the other, it is possible to change both the pressure and the temperature within certain limits, and still have the same number of liquids. In gases, of course, there can be only one phase, since they mix in all proportions. When a solid has several allotropic states, they form as many different solid phases. Thus, the possible phases of sulphur are rhombic sulphur, monoclinic sulphur, liquid sulphur, and sulphur vapour. Any of these by itself is bivariant. There are six univariant systems, and four invariant systems, such as the solid sulphurs, with the vapour or the liquid; or one of them with liquid and vapour. If, as appears probable, there are more than two solid phases in sulphur, an invariant system may be obtained by means of three of these, without the liquid or vapour.

CHEMICAL CONSERVATISM

It should be remembered that the Phase Rule is a statical, and not a dynamical, principle. It only applies to states of equilibrium, and not while changes, however gradual, are going on. This consideration is emphasised by the "reluctance" of bodies in general to form new phases. We all know the slowness with which freezing and boiling set in. Condensation requires nuclei. Liquefaction alone seems to encounter no resistance. There is super-cooling, or superheating of water, but no super-heating of ice. It has even been suggested that the diamond is a "metastable" form of carbon, whose reluctance to change its phase is the only cause why it does not change into graphite. This "metastability" appears to increase with the valency of an element. An element of high valency is one which has a large number of "linkages"—in other words, a large number of chances for taking up or discarding electrons. It is quite conceivable, therefore, why it should form chains and groups whose configuration would tend to preserve the state of aggregation in which they happen to be.

A general expression of this reluctance to change a state is known as the theorem of Le Chatelier. It is stated by Ostwald as follows: "If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, i.e. one by which its effect is partially annulled."

This theorem has a most suggestive bearing upon the problems of biology. It is one of those few general principles which seem to extend throughout the field of science. In life-phenomena we find this defence of the organism against a disturbing influence. In electricity we find it again in the phenomena of induction. In mechanics we find it in the equality of action and reaction.

Van't Hoff, in his "Studies in Chemical Dynamics," pointed out that when a system is in equilibrium, and its temperature is raised, any reaction which takes place reduces the temperature, or, at all events, absorbs heat, and vice versâ. Again, when the pressure is increased, any reaction which takes place tends to reduce the volume. This, under ordinary circumstances, would increase the pressure.

These laws, and the general principle of conservatism apply to all systems and changes of the condition of equilibrium, whether physical or chemical; to evaporation and fusion; to solution and chemical action. The changes which do occur show another peculiarity. They do not pass from one state to the most stable state suitable for the new conditions. They prolong the agony as much as possible, passing from the most unstable state to the more stable, and gradually to the most stable. Sulphur vapour, cooled at the ordinary temperature, first of all condenses the drops of liquid, which solidify in an amorphous form, and gradually crystallise. When phosphorus vapour is condensed, white phosphorus is formed first, and the more stable red phosphorus afterwards. Even when sulphur crystallises from its solution in benzene or carbon disulphide, the monoclinic form is found to crystallise * out first, and afterwards the rhombic form.

CONCENTRATION

Besides the temperature and pressure, a third element of variability is the concentration, or the amount of a substance contained in unit volume. When no other substance is present, the concentration is identical with the density. In the preparation of alloys, the temperature and concentration or proportion of the ingredients are, as a rule, more important than the pressure. The so-called "cryohydric" or "eutectic point" is the lowest temperature obtainable by an alloy from given substances in the presence of their vapours.

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* See *The Phase Rule*, by A. Findlay. Longmans.

Raoult's simple rule that "the freezing-point of a liquid is depressed by dissolving a substance in it, and the depression is proportional to the amount of substance in solution," has of late been considerably modified. We must now take into account the solution of gases in liquids, of gases in solids, of solids in solids, and of liquids in each other (as, for instance, of two fused salts).

If two substances form an unbroken series of "mixed crystals," or solid solutions, there can only be one solid phase, since the solid phase is homogeneous. There can also be only one liquid phase, and, since all gaseous phases are homogeneous, we can never have more than three phases in any system of two bodies which mix evenly in all proportions. Since, in applying the phase rule to this case, $C = 2$ and $P = 3$, we have $F = 1$, and the system can never become invariant. Hence the freezing-point curve must be continuous, and there is no "eutectic point." The melting-point curve is, in harmony with the "conservatism" above referred to, somewhat higher than the freezing-point curve on a diagram which gives these points in terms of the "concentration," or relative composition, of the alloy. It has lately become usual to call the freezing-point curve the "liquidus," and the melting-point curve the "solidus." The gold-platinum curves are notable as forming nearly a single straight line.

OPTICAL ACTIVITY

An interesting application of the phase rule is to the solution of the vexed question as to whether certain optically inactive substances consist of mixtures of two substances, one of which rotates the plane of polarised light to the right, while the other rotates it to the left. The constitution of mandelic acid has recently been solved by Adriani by a study of its fusion-point in the light of the phase rule.

As is generally the case in all scientific achievement, the whirl of phenomena becomes more complex the greater the detail which comes within our ken. Every increase of discriminating power means an increase of complexity. But, although many previous generalisations have to be abandoned in the light of the new knowledge, new laws are discovered, which serve not only to bind the new facts together, but to shed a clearer light on the connection existing between phenomena previously regarded as unrelated.

CHAPTER V

OPTICAL CHEMISTRY

THE progress of chemistry is to a great extent an emancipation from misleading optical effects. Appearances are nowhere so deceptive as they are in our endeavour to classify chemical substances by their visual characters. Hundreds of gases and vapours are colourless and transparent; so are the majority of solutions, and a vast number of organic liquids. Even in the solid state, the close resemblance of some precipitates presents many a puzzle to the analyst. Although the colour of a precipitate, or of a Bunsen flame, gives us a good rough-and-ready indication of identity, and a discoloration is a valuable index in quantitative analysis, it is significant that the most delicate researches of recent chemistry have been carried out with certain advanced optical reactions of extreme sensitiveness. Chemists use the spectroscope, the microgoniometer, the polarimeter, the Zeeman apparatus, and the ultra-microscope as regular adjuncts to the up-to-date laboratory. Instead of taking the naked-eye appearance of substances for their guide, they borrow from the physicist his most delicate optical contrivances, and study the more detailed and characteristic appearances revealed by their means. Whole new departments of chemistry have thus arisen, and the result has been to obliterate still further the frontiers between physics and chemistry.

The optical tests applied to substances are numerous, and are increasing rapidly. In the case of gases we have the spectra of emission and absorption, as well as the refractive index. In liquids we have, in addition, the magnetic and the natural rotation of the plane of polarisation. In solids we have double refraction and the numerous reflection phenomena, together with all the tests applicable to gases and liquids. All these are now standard tests. Others, like the Zeeman and Hall effects, and the Brownian motions, will probably soon come into general use.

OPTICALLY ACTIVE LIQUIDS

That a liquid should rotate the plane of polarisation of a beam of light passing through it is one of those anomalies which fly in the face of all our prejudices. To us, it appears absurd to associate any idea of rotation with the liquid state except a rotation of the liquid as a whole or a vortex motion. But neither would account for the rotation in question. If we look at a spinning liquid mass along the axis of rotation, say, from above, the rotation appears either right-handed or left-handed. Looked at from below, it appears reversed, just as is the motion of the hands of a clock as seen through the back of a transparent dial. In the magnetic rotation of the plane of polarisation, usually called the "Faraday effect," the same rule holds good. The rotation is right-handed or left-handed, according to the point of view.

But in "natural" optical rotation the case is different. In whatever direction the beam of plane-polarised light travels through the liquid, its plane is twisted in the same sense. This twist may be annulled by reflecting the beam back through the liquid. If two tourmalines or Nicol prisms be crossed, so as to extinguish all transmitted light, the light will shine out again as soon as an optically active liquid, such as turpentine, malic acid, or sugar solution, is introduced between them. To extinguish the light again, the second tourmaline or Nicol must be turned through several degrees. If, in looking towards the source of light, the analysing tourmaline or Nicol has to be given a right-handed twist, like an ordinary screw, the liquid is called "dextro-rotatory"; if in the opposite direction, "lævo-rotatory." If a substance occurs both in the dextro and lævo forms, the former is called the *d*-form, and the latter the *l*-form, and a mixture of both is called a *dl* mixture.

The amount by which the plane is rotated is characteristic of each substance, and is of supreme importance. Instruments for accurately measuring the "specific rotation" have been devised by Mitscherlich, Wild, Laurent, Lippich, Soleil, Landolt, Poynting, and many others. They are called polariscopes, polarimeters, polari-strobometers, or saccharimeters, and many of them are marked by great ingenuity and precision. As usual, the commercial value of these instruments (in sugar-refining, the diagnosis of diabetes, etc.) has reacted favourably upon their scientific development.

The actual rotation depends upon the thickness of the liquid layer traversed. In *l*-turpentine the specific rotation (or rotation divided by specific gravity) is 36° per decimetre, or 3·6° per cm. It is usual to take the decimetre as the standard thickness, since it offers convenient angles for most substances. In pure nicotine, which is lævo-rotatory, the specific rotation is as high as 161°, and in that extraordinary substance, Santonid, $C_{15}H_{18}O_3$, it reaches the enormous value of 991° in the green part of the spectrum.

OPTICALLY ACTIVE CRYSTALS

We are so accustomed to the influence of crystals upon light that it does not surprise us to find optical rotation in them also. Crystals are, after all, those bodies in which the play of light gives us the most delightful variety and brilliance. Their refraction and dispersion are, on the whole, much greater than what we find in liquids. And their optical rotation, where it does occur, is correspondingly great. It is, in fact, about a hundred times more intense. In chlorate of sodium it is some 3°, not per decimetre, but per millimetre, of thickness traversed. In quartz it ranges from 12° in the extreme red to 70° per mm. in the ultra-violet, and observations with cadmium lines have reached values as high as 236° per mm. The hyposulphates of lead, potassium, and strontium, the tartrates of rubidium, and the hydrated sulphate of strychnine are among other crystals which show decided rotation.

ROTATION OF TOURMALINE BY LIGHT

A converse effect of great interest appears to have been discovered quite lately by J. A. Anderson.* If a plate of tourmaline, cut in the usual way, is suspended so that it partly absorbs the light from a plane-polarised beam, it tends to place itself in such a position as to absorb the light more completely. If the axis of rotation lies in the beam of light, and the crystalline axis is placed at 45° to the plane of polarisation, the axis will tend to place itself at right angles to the same plane and thus absorb all the light. This is an instance of the working of the "law of maximum entropy." Energy always tends to reduce itself to its lowest form, viz. heat, and a portion of it may be expended in bringing about a change which accelerates the degradation of energy. The Anderson effect is a striking illustration of this law, although it must be admitted that the mechanism by means of which this mechanical rotation is brought about is far from clear.

THEORETICAL CONSIDERATIONS

In crystals the rotation of the plane of polarisation is nearly accounted for. Their molecules are probably arranged in such a manner that their electrons revolve more easily in one sense than in another, and that this laxity comes most into play when the beam of light traverses the molecule in a certain direction. The substances whose crystals exhibit optical rotation are none of them very simple, and the crystals consist, no doubt, of closed systems, each comprising many molecules, giving as many different directions in which the difference of laxity referred to may come into play. Whichever way the plane-polarised beam may be traversing the crystal, there will always be a certain proportion of molecules which retard one circular component more than the other. This, as shown in my *Electron Theory*, explains the rotation of the plane of polarisation. For a plane-polarised beam is equivalent to two circularly polarised beams of opposite signs. If one of these is retarded, while the other is accelerated or unaffected, the result is a rotation of the plane of the recombined beams.

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* See *Nature*, 78, p. 413, September 3, 1908.

Suppose that a circularly polarised beam of light enters a medium in which there are a number of electrons revolving in orbits in the same sense as the beam of light. In accordance with the principle of induced currents, all the electrons will be retarded, and will describe their orbits with a somewhat reduced frequency. The disturbance will affect the rate at which the polarised beam is transmitted through the medium. Each electron will give a set-back to it, and the final effect will be that the polarised beam will describe fewer revolutions about its own axis after traversing the medium than it would have done after traversing so much empty space.

If the electrons revolve in the opposite direction, the beam is accelerated instead of being retarded.

Such accelerations and retardations are not as purely "theoretical" as they may appear to be. Any revolving electric charge emits a circularly polarised "beam" of electromagnetic energy, which, on reaching a certain amplitude and frequency, becomes visible as light. In the Zeeman phenomenon, the molecular currents of magnetism are used to accelerate and retard the electronic orbits of sodium atoms, and this difference of frequency appears as a doubling of the spectrum lines. We are, therefore, in touch with fact in more directions than one.

SPIRAL ORBITS

But, so far, we have not accounted for the curious fact that even in an apparently isotropic liquid the plane of polarisation is rotated in the same sense whatever the direction of transmission. Obviously this is not a matter of electronic rotations preferably in one direction. In the first place, a rotation in one sense would be doubled if the beam were reflected and returned along its path, as is actually the case in the Faraday effect; whereas in "natural rotation" the effect is annulled by reflecting the beam along its old path.

Also, even if the liquid gave a rotation in one sense in a certain condition, everything should be changed by stirring the liquid. But no such thing takes place. We are, therefore, driven to the conclusion that the phenomenon is a molecular one, and we must look to some dissymmetry in the molecule itself to account for the optical preference it exhibits.

We must conclude that the electronic motion which affects the beam of light—and nothing else ever does affect it—is not confined to a space of two dimensions. For if it were, both its aspect and the direction of the beam would be reversed simultaneously, and a final result of a to-and-fro path would be a double rotation in the same direction.

There must be no such plane of symmetry. The orbit or path of the disturbing electron must be tri-dimensional. Drude, in his *Optics*, showed that spiral orbits would account for the rotation observed. Such orbits would be produced if one atom, carrying with it one or more revolving electrons, itself revolved round the centre of gravity of the molecule. Such a structure would have a "preferential rotation" in three-dimensional space, irrespective of its orientation. An approximation to such a state is shown on a large scale by the satellite system of Uranus.

Another electronic arrangement which would also explain the facts would be one in which the electrons, instead of revolving, oscillate in short lengths of a spiral path having the shape of a right-handed or left-handed screw. Such a path is more difficult to conceive theoretically, but it should be borne in mind for further consideration.

UNSYMMETRICAL CARBON

So far the electron theory. It is a tunnel bored into a rock of fact from one side. Another tunnel is being bored from the purely chemical side. Will the tunnels meet?

The optically active liquids *all* contain one or more of a limited number of elements. Among these carbon is supreme, being the dominant constituent of almost all the optically active liquids hitherto discovered. Sulphur, tin, selenium, and silicon are also capable of giving rise to optically active liquids, like the yellow oil obtained from tin, which is styled methyl-ethyl-*n*-propyl stannic iodide. But although these other elements are the essential active constituents, the active compounds have not been obtained free from carbon, which would, after all, be more satisfactory.

Carbon, then, is the optically active element *par excellence.* And the most important property which enters into consideration here is the isomerism of carbon compounds.

Carbon is quadrivalent. It combines with four hydrogen atoms to form methane, CH_4. Each of these four atoms must be attached in some way to the carbon atom. The only symmetrical way in a space of three dimensions is to let their centres form a regular tetrahedron. We thus get the tetrahedron, the basis of the new science of stereo-chemistry.

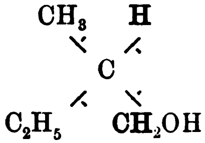
A tetrahedron has some very peculiar and significant properties, which are best understood by constructing a model with cardboard, or cutting it out of wood or soap. Let its points be labelled *a*, *b*, *c*, and *d* respectively. Then it is found that the letters can be distributed in two essentially different ways, and in two ways only. If, on looking at one face, the letters *b*, *c*, *d* read round in a right-handed direction, it is impossible to obtain a direct aspect in which they read round in a left-handed direction. And the same remark applies to any other combination of letters. If a *c* is substituted for the *d*, the combination *a*, *b*, *c* can be read in either direction.

This geometrical fact has an important chemical application. If a carbon atom is combined with four different atoms, or groups of atoms, these may be arranged round it in two, but not more than two, essentially different senses. The two substances thus produced are identical in composition, but *they rotate the plane of polarisation in opposite directions.*

STEREO-CHEMISTRY

Van't Hoff and Le Bel were the first to apply such geometrical considerations to the structure of carbon compounds, although Wislicenus already in 1873 pointed out the necessity of regarding chemical formulæ from the three-dimensional point of view.

A typical case of an optically active compound is amyl alcohol, which may be written thus:



Here, the groups joined to the four valencies of carbon are all different, so that we have a clear possibility of two different arrangements, giving rise to two so-called "stereo-isomers." When there are more central carbons than one, the number of possible isomers increases.

When two "antipodes," or opposite stereo-isomers, combine into a single substance, such a compound is called a "racemic" compound. It has no optical activity. Neither has an equal *dl* mixture of the two antipodes; but the mixture may be distinguished from the compound by an application of the Phase Rule, as already mentioned.

LIFE AS A STEREO-CHEMICAL PHENOMENON

It is a remarkable and suggestive fact that the majority of substances elaborated by the animal organism are optically active. Also, when a non-active substance is absorbed it is, as a rule, converted into its active stereo-isomers, if such exists. It has been suggested that, since the vital processes take place comparatively slowly, there is time for certain natural forces of rotation, such as that of the earth, to come into play. However that may be, it is certain that the living organism is capable of discriminating between dextro and lævo-compounds without having recourse to the polariscope.

Cocaine is a drug used to produce local anæsthesia. It has two stereo-isomeric forms. Of these, the dextro-cocaine is the stronger. It paralyses the tongue more rapidly, although its effect is less lasting than that of lævo-cocaine.

Quinine is lævo-rotatory. Dissolved in alcohol, it rotates the plane of polarisation 171° per decimeter of 1 per cent solution. Its stereo-isomer quinidine is dextro-rotatory, and is not narcotic; but both are good febrifuges.

Lævo-nicotine is twice as poisonous as dextro-nicotine. Injected into the blood, it causes great pain, followed by paralysis, spasms, retardation of the heart's action, and finally death by asphyxia. Dextro-nicotine, when injected, only causes a strong shivering fit, which soon passes.

Curare, the poison of Central American poisoned arrows, is a nitrogen compound in which all the five valencies of nitrogen come into play. It has an acute paralysing action on the muscles. This action is, however, common to many other substances; and what is common to them is that the configuration of their molecules is necessarily tri-dimensional. Certain organic compounds of phosphorus, antimony, and arsenic are known to act like the curare poison. They are all quinquivalent. Sulphur is, generally speaking, bivalent, and low-grade compounds like SO_2 must be confined to a two-dimensional arrangement, since there are only three atoms in the molecule, and a plane can always be laid through their three centres. But when, for instance, alkyl iodides are combined with the sulphides, we at once get optically active forms, implying a tri-dimensional arrangement. One such compound, known as trimethyl-sulphine hydroxide, with a formula $(CH_3)_3.S.OH$, has a pronounced curare character.

Again, malic acid (the acid contained in apples, pears, rhubarb, and the berries of the mountain ash), when heated to 180° C., gives rise to two stereo-isomers of the formula $C_4H_4O_4$, termed respectively, fumaric and maleic acid. The former is a much feebler poison than the latter. The organism is well able to discriminate. In some cases one isomer has a strong taste—like peppermint, let us say—while the other is quite tasteless.

The importance of geometrical arrangement has been brought out by a brilliant series of researches conducted by Prof. P. F. Frankland in Birmingham, especially on the tartrates and tartramides. The substitution of aromatic radicles in the latter gives higher dextro-rotations than the substitution of aliphatic radicles, and in the former the "para" arrangement is much more powerful than the "ortho" arrangement.

STERIC HINDRANCE

An important expansion of stereo-chemistry has lately been made in a direction in which isomerism does not come into play, but in which considerations of space (in a non-journalistic sense) play a determining part. Many reactions can be calculated from the known affinities of the substances brought together. Those which belong together seek each other out and combine more or less rapidly; but when the molecules become more complex, it may happen that the kindred spirits cannot get at each other, simply because a crowd of other atoms block the way. That is Steric Hindrance. If, in a substance like acetone, all the hydrogen atoms are replaced by methyl radicals, we obtain a substance much more difficult to subject to further modification. Certain acids derived from benzoic acid may be given great stability by substituting chlorine or methyl for hydrogen atoms in certain positions. It then becomes very difficult to convert them into esters (or compound ethers) by the usual means. According to Bischoff's Dynamic Hypothesis, the atoms always endeavour to take up positions which give the most scope for vibration. This is another instance of the law of maximum degradation of energy, since the electrons associated with the atoms are thus enabled to waste the largest amount of energy in the form of radiant heat.

FUTURE PROBLEMS

In his admirable treatise on *Stereo-chemistry* (Longmans, London, 1907), Dr. A. W. Stewart says (p. 532): "The problems of optical activity, which first led to the introduction of special ideas into chemistry, seem now to be passing into a new stage, and to be treated more from the point of view of the physicist than from that of the pure chemist." This is part of the general tendency already observed. Other problems are more purely chemical. "For example, the phenomena of racemisation . . . are not even yet completely clear to us. We know that certain active compounds may be racemised by heat, and we draw the deduction that during this process changes take place in the arrangements of the atoms in space; but we have no idea of the nature of this arrangement. . . . The solution of such a question as this would lead to most valuable results, as it would enable us to decide, once for all, the problem of 'directed' as opposed to 'undirected' affinities."

The only light dawning at present over that scene is whatever new information we can obtain concerning that mysterious "positive nucleus" of the atom to which Sir Joseph Thomson referred at Winnipeg. Once we know its structure, it will be comparatively easy to interpret chemical affinity. It looks like being resolved, after all, into magnetic force between molecular electronic orbits. Such forces are certainly "directed," changing rapidly from the axial to the equatorial positions. Let us hope that the light may come soon.

CHAPTER VI

THE THEORY OF SOLUTIONS

THE vast majority of chemical processes are carried out in the liquid state. Two liquids are more easily mixed than two powders, and they are more easily manipulated than two gases. This ease of mixture and manipulation facilitates the control of the processes, and saves time in the reactions. Hence, also, the popularity of the "wet way" in chemical analysis.

No department of chemistry has advanced more rapidly within the last generation than the theory of solutions. The names of Van't Hoff, Arrhenius, and Ostwald are associated with what must be styled a revolution in the chemistry of liquids.

TWO CLASSES OF LIQUIDS

In 1894, Ramsay and Shields proved, by measurements of the surface tensions of liquids, that they can be divided into two classes. In one class of liquids, the molecules are as simple in the liquid as they are in the gaseous state. In the other class, the molecules form groups or chains within the liquid. The most notable example of the second class of liquids is water, which is the solvent of solvents, the real "alkahest," if any such exists. Only a few substances, such as the alcohols, benzol, acetone, and carbon bisulphide can even remotely compare as solvents with water. The great majority of liquids belong to the first class.

SURFACE ENERGY

The peculiar power of water to dissolve substances appears to be due to its complex internal structure. We must imagine the molecules of water as forming structures, each consisting of many molecules, and capable of exerting a force sufficient to break up the cohesion of the molecules of the solid. This cannot be done without the expenditure of a certain amount of energy, and this energy is partly derived from the heat of the water itself. If we knew accurately the number of molecules in, say, a grain of common salt, and their arrangement in the salt crystals, we could calculate the amount of energy required to overcome its cohesion from the known value of its tensile strength. An approximate value of this energy may be obtained from the latent heat of fusion, which is also a process in which the contact between the molecules of solid salt is loosened.

Now the latent heat of fusion of 58·5 grams (or one gram-molecule) of NaCl is 5 kilogram-calories. In other words, it takes an amount of heat capable of raising the temperature of 5 kilograms of water 1° Centigrade to melt one gram-molecule of salt. To dissolve the same amount of salt in 100 gram-molecules of water (=1800 grams), requires 1·3 kilogram-calories, besides whatever hidden energy the water molecules can supply. This hidden energy is the energy with which the salt molecules take up their appointed positions among the water molecules. It must amount to 3·7 kilogram-calories to make the balance even. Thus we have the following balance-sheet of energy.

Required for solution, 5 kgr.-cal. Supplied by internal energy, 3·7 kgr.-cal. Supplied by external heat, 1·3 kgr.-cal.

In other cases, such as the solution of quicklime or sulphuric acid in water, the difference between internal energy and energy of liquefaction is positive, and the water, instead of being cooled, is heated. But the salts which cool water on dissolving in it are in a decided majority.

If salt were constantly being dissolved in water, we should have an expenditure of, say, 4 horse-power for liquefying the salt, i.e. breaking up its cohesion. Of this power 3H.P. could be recovered by letting the salt diffuse through water, but the balance of 1H.P. would have to be constantly supplied from without.

We must picture to ourselves, then, the water molecules in contact with the salt molecules, constantly engaged in pulling the latter out of their positions of equilibrium. The surface-energy of water—exhibited by its high capillarity, among other things—is particularly suitable to this work.

DISSOCIATION OF VAPOURS

But water does more than break up the solidity of the salt crystals. It also breaks up the cohesion of the salt molecules themselves, and actually separates the sodium from the chlorine in a large proportion of them.

This phenomenon, first studied by St. Claire Deville, was originally observed in certain vapours. The favourite case of vapour dissociation is that of sal-ammoniac, or ammonium chloride, which on heating is partly decomposed into chlorine and ammonia. These two constituents may then be separated by diffusion. Iodine vapour, which has a vapour density of 8·8 (air = 1) at 650° C., has a little over half that density at 1500° C., and under the same pressure. Since the atom of iodine is 9 times as heavy as that of nitrogen, a vapour density of about 9 would be just right if iodine, like nitrogen, existed in molecules containing two atoms each. Half that density indicates that the iodine has become monatomic under the influence of heat.

The energy required for this dissociation is very considerable. Boltzmann has calculated it to be 28·5 kilogram-calories for one gram-molecule (= 254 grams). When acetic acid undergoes a similar dissociation, it consumes 20 kilogram-calories per gram-molecule.

When the temperature falls, this dissociation is annulled, and the substance returns precisely to its previous state, nor does a frequent repetition of the dissociation make any perceptible difference.

ELECTROLYTIC DISSOCIATION

These facts prepare us for an important extension. Dissociation takes place in solutions as well as in vapours. In 1883, Svante Arrhenius was carrying out an investigation into the conductivities of different electrolytes, when he found certain parallelisms between the chemical activity and the electrical conductivity of substances. The "strongest" acids, i.e. those which displace most other acids from their salts, are also the best conductors when dissolved in water. The velocity of a chemical reaction is proportional to the conductivity of the acid used. Pure anhydrous hydrochloric acid does not attack oxides or carbonates. It is also an insulator. We know already that pure sulphuric acid may be transported in iron bottles.

Beginning, then, with pure anhydrous HCl, a non-conductor, we may add more and more water to it, and the more water we add, the greater will be both the "strength" of the acid and its electric conductivity, up to a certain limit. As dilution proceeds, more and more HCl molecules are dissociated into H and Cl, and it is these loose wandering atoms, called "ions" by Faraday, which conduct the electric current.

When the concentration of the hydrochloric acid has become "milli-normal," i.e. when one-thousandth gram-molecule of HCl is contained in each litre of water (giving a percentage of 0·00365), quite 99 per cent of all the HCl molecules in solution have become dissociated, and the acid has almost reached the limit of its specific conductivity.

That this interpretation is correct may be seen by cataloguing the conductivities for various dilutions. If the current were conducted by the molecules, the specific conductivity should decrease with increasing dilution, and should always be proportioned to the amount of acid in solution. But such a "linear" variation of the conductivity only sets in when the dilution is extreme. When all the molecules are dissociated, any further dilution simply diminishes the average number of carriers of electricity found in unit volume.

We must next ask ourselves why the dissociation should increase with increased dilution. The answer is simple. There is a constant dissociation and recombination of ions. The former is produced by the activity of the water molecules, and is, as we might expect, increased by heat. The recombination is due to the electric attraction between the ions. For all the chlorine ions are negatively charged, and all the hydrogen ions positively. The charge is the same in each case, but for the reversal of sign. It is that of a single electron. In parting company with the hydrogen atom, the chlorine atom deprives it of one electron. Hence, both charges.

The rate of recombination of ions in a given volume is proportional to the number of H ions present, and also to the number of Cl ions present. Since both are present in equal numbers, the rate of recombination is proportional to the square of one of the numbers. It is, in fact, proportional to the number of encounters between opposite ions. For somewhat similar reasons, the marriage rate is highest in densely populated districts.

These collisions become less frequent as dilution proceeds, whereas the process of dissociation continues unabated.

MORE PARALLELISMS

It might seem at first sight difficult to prove that metallic sodium and uncombined chlorine exist in a dilute solution of hydrochloric acid. Even more difficult might it appear to make it plausible that a trillion charged atoms of each kind are disseminated through every cubic centimetre of a 0·00365 per cent solution of hydrochloric acid. If that were so, one might exclaim: Could not these ions be drawn to one side or the other by simply bringing the solution into an electric field, or into the neighbourhood of any charged body? The answer is: They could. But the field would soon be neutralised by the ions of the opposite signs accumulating at each end, unless there were some contrivance for taking up their charges. If there were such a contrivance, we should have what we are already familiar with, viz. electrolysis. It is by just such a process of drawing ions in opposite directions and discharging them, that acidulated water, let us say, is decomposed by the electric current.

But the theory of electrolytic dissociation could hardly have made such rapid headway had it not been confirmed by the most diverse analogies. Raoult found that when a non-volatile substance is dissolved in water the boiling-point is raised, and the rise is strictly proportional to the number of molecules in solution. This rise in the boiling-point is connected with the attraction between the water molecules and the molecules of the dissolved substance, an attraction which, as we have seen, is responsible for a very appreciable amount of work performed.

Here, again, we might expect the rise in the boiling-point to be proportional to the concentration of the salt in the water. But when careful measurements are made at various dilutions, it is found that the rise diminishes too slowly with diminishing concentration. In fact, it is the story of electrolytic conductivity over again. There are too many molecules, and the only resource is to suppose that the dissolved salt has been dissociated.

Other confirmations abound. There is a depression in the freezing-point as well as a rise in the boiling-point, and its indications, so far as they go, also point to dissociation. Then we have refraction. The refractive index of a liquid is altered by dissolving another substance in it. The change is so characteristic of the substance dissolved that tables of "molecular refractions" have been compiled for a large number of bodies. These refractions also exhibit anomalies which point to the dissociation of salts at high dilutions.

CHAPTER VII

OSMOTIC PRESSURE

ALL these various facts were brought into clear relation with each other as soon as the laws of osmosis became accurately known.

When a glass tube, open at one end, is nearly filled with a strong solution of sugar (water can hold twice its own weight of cane-sugar), closed with an animal membrane, and inverted into a vessel filled with water, the sugar solution is seen to rise in the tube against the pressure of the air imprisoned in it. It compresses the air with considerable force, and the pressure on the membrane eventually bursts it. This kind of pressure is called Osmotic Pressure.

Osmotic pressure increases with the concentration of the solution, and is, in fact, exactly proportional to the number of molecules of the dissolved substance in unit volume of the solution. We may make it as small as we please by making the solution sufficiently dilute. This gives us a means of measuring the osmotic pressure without destroying the membrane. The most perfect membranes are those which allow water to pass through them freely, but not the sugar. The best-known membrane of this kind is the "semi-permeable" membrane invented by Pfeffer in 1877. It consists of a film of ferrocyanide of copper, made in the following manner: A porous earthenware pot is placed in water, and water is sucked through its pores until they are quite free from air. It is then filled with a solution of potassium ferrocyanide ("yellow prussiate of potash"), and immersed in a bath of sulphate of copper. The two solutions meet in the walls of the cell, and where they meet, ferrocyanide of copper is precipitated in a colloidal form. It makes a film whose thickness gradually increases, and behaves very much like a living cell-membrane, in that it allows water to pass freely, but not salt, sugar, glycerine, or similar substances.

When such a membrane is used for closing the glass tube, the osmotic pressure of the solution may be measured by observing how much the air in the upper part of the tube is compressed. If the levels were originally the same outside and inside the tube, and the volume of air imprisoned in the tube is reduced to one-half, when no further rise takes place, it means that the solution is under an osmotic pressure of one atmosphere, for, according to Boyle's law, air reduced to half its volume exerts double its former pressure. The pressure of the imprisoned air is two atmospheres, and of the outer air, one atmosphere. The difference is the "osmotic pressure," or the pressure required to prevent more water entering the solution.

VAN'T HOFF'S LAW

Now, the numerical value of this pressure offers a most singular and suggestive analogy to gaseous pressure. It happens to be the same pressure as that which would be exerted by the dissolved substance (the "solute") alone, if the solvent were suddenly withdrawn, and the molecules of the solute were left, like gaseous molecules, flying at random in the space formerly occupied by the solution.

Let us reduce this to figures. A 3·42 per cent solution of cane-sugar in water has an osmotic pressure of 2·41 atmospheres. That pressure is required to prevent it diluting itself with water. The solution specified is a "decinormal" solution. For the formula of cane-sugar is $C_{12}H_{22}O_{11}$, and as the atomic weights of the constituents are $C=12$, $H=1$, O = 16, the molecular weight is 342. Hence, a gram-molecule of cane-sugar weighs 342 grams, and a normal solution is one gram-molecule dissolved in one litre, or 1000 grams of water. A normal solution being one of 34·2 per cent, a deci-normal solution will be one of 3·42 per cent, as stated. And this has an osmotic pressure of 2·41 atmospheres.

Now, according to the principle of Avogadro, a unit volume of every gas contains the same number of molecules, under standard pressure and temperature. In other words, the density of a gas is a measure of its molecular weight. Or, again, the pressure exerted by a given weight of gas contained in unit volume is proportional to the number of molecules—i.e. inversely proportional to its molecular weight. Taking a gram-molecule of each gas, we shall always, therefore, get the same pressure by confining it in a standard volume at standard temperature. If the standard volume is one litre, the gram-molecule of any gas exerts a pressure of 24 atmospheres. A tenth of a gram-molecule exerts one-tenth of that pressure—viz. 2·4 atmospheres. Could we volatilise cane-sugar without decomposing it, it would also, in the gaseous state, exert this pressure. A deci-gram-molecule per litre would exert a pressure of 2·4 atmospheres, or the same pressure as its *osmotic pressure* when dissolved in water.

This analogy is so important that it may be well to arrive at it in another and, perhaps, a simpler way. Consider the pressure of one cubic cm. of air. Under ordinary conditions it is one atmosphere. It weighs 1·23 milligrams at 14° C. A 1·42 per cent solution of cane-sugar has an osmotic pressure of one atmosphere. One cubic cm. of such a solution contains (very nearly) 14·2 milligrams of cane-sugar. These weights, 1·23 and 14·2 are just in inverse proportion to the molecular weights of air and sugar respectively. The former is, on the average (of oxygen and nitrogen), 28·8, while the latter has a molecular weight of 342, as we have seen. The cubic cm. of solution, therefore, contains as many molecules as the cubic cm. of air, and its osmotic pressure equals the gaseous pressure.

We may make it even clearer by calculating the number of molecules concerned in each kind of pressure. The number of molecules contained in any gas under standard conditions has been estimated as between $3{\cdot}6 \times 10^{19}$ and $4{\cdot}0 \times 10^{19}$ per cub. cm. Let us say $3{\cdot}8 \times 10^{19}$. What is the number of sugar molecules contained in 1cc. of aqueous solution of osmotic pressure equal to one atmosphere?

The amount of sugar present is 14·2 milligrams, as stated above. The weight of an atom of hydrogen being $1{\cdot}1 \times 10^{-24}$ grams, that of a molecule of cane sugar will be 342 times that amount, or 376×10^{-24} gram. This weight is contained in the weight of sugar $3{\cdot}78 \times 10^{19}$ times. Hence, there is that number of sugar molecules in the solution exerting one atmosphere of osmotic pressure, or the same as the number of molecules in 1cc. of a gas under atmospheric pressure.

This remarkable fact was generalised by Van't Hoff in 1887 into the following important law:—

"The osmotic pressure of a solution equals the pressure which the solute would exert if it were contained as a gas in the same space as that occupied by the pure solvent."

The osmotic pressure is, like the pressure of gases, proportional to the absolute temperature.

INTERPRETATION

Van't Hoff's great law has experienced some hesitation in its acceptance, owing to the loose way in which it is often stated. Worded as above, it simply expresses an experimental fact, or, rather, an immense array of experimental facts of the widest range. But some enthusiastic advocates of the kinetic theory of liquids are apt to go further, and to say that the sucking in of the water into the solution is due to the osmotic pressure *exerted* by the molecules of the solute. It then becomes difficult to conceive how a pressure can produce a suction, or how a pressure of several atmospheres, exerted upon the inner walls of a vessel, can make water flow into the vessel from without. Van't Hoff's law asserts no such thing. It simply states that the additional pressure required to keep more water from entering the solution equals the pressure of the substance already dissolved, considered apart from the solvent.

SEMI-PERMEABLE AIR.

The matter becomes much clearer when we consider air as a semi-permeable substance. We know already that the vapour pressure of a solvent is lowered by dissolving a substance in it. Let two open vessels be placed side by side, one containing pure water, and the other containing sugar solution. At any given temperature, the vapour pressure of the sugar solution is less than that of pure water. Hence, vapour given off by the latter is condensed by the sugar solution. To prevent this, we must increase the pressure on the pure water, and this additional pressure may also be regarded as a kind of osmotic pressure, although it never amounts to more than a small fraction of an atmosphere. The air, in this case, acts as a semi-permeable substance, transmitting water, but not sugar.

On the whole, perhaps, the term "osmotic pressure" was not well chosen. More fitly it might have been called "anti-osmotic pressure," or "anti-dilution pressure." Certainly, the solute does not increase the pressure upon the vessel from within. If anything, it reduces it. It certainly reduces the internal pressure of the liquid, as well as the vapour pressure. We might define the osmotic pressure as the amount by which the internal pressure of a liquid is reduced by dissolving a substance in it. We do not yet know sufficient of the internal constitution of liquids to be able to say why the dissolution of a substance should diminish the internal pressure of a liquid. If the water and the solute form complex molecules together, or molecular chains of greater complexity than those of pure water, it is quite intelligible that the internal pressure should be reduced. In gases, the dissociation of molecules by heat increases the pressure, and their recombination or "polymerisation" reduces the pressure. It is a case of Avogadro's principle.

When the internal pressure of a liquid is reduced, a liquid of greater internal pressure will easily penetrate into it. Hence, the "suction" of the solvent through the membrane into the solution.

We may look upon the matter in this way. The molecules of pure water press into the membrane from one side. The molecules of the solution press into the membrane from the other. When the solution is infinitely dilute, every water molecule finds itself face to face with another water molecule of equal energy on the other side. But on adding the solute, every molecule of the latter places one molecule of water out of action, so that it can no longer keep the intruding water molecule at bay. The internal pressure of the solution is thus reduced in exactly the same way as if the molecule of solute removed one molecule of water. The pressure will thus be reduced by the amount due to as many water molecules as have been thus removed or put out of action. This is equal to the number of molecules of the solute, and these, by Avogadro's principle, exert the same pressure as the molecules of any other substance. Hence the reduction of internal pressure is equal to the pressure due to the sugar molecules, and is the same as the pressure the latter would exert if they filled the same volume in a gaseous state. This presentation of Van't Hoff's law, though omitting many peculiarities of the liquid state, covers the facts observed, and has the advantage of making the law fairly intelligible. It must be remembered, however, that very little is yet known concerning the internal structure of liquids.

MOLECULAR WEIGHTS

The importance of Van't Hoff's law lies at present not in its bearing upon a future theory of liquids, but in its practical applications, which extend through nearly the whole of chemistry.

Arrhenius does not hesitate to call it "one of the most general laws of matter." It must be admitted that the law has been invaluable in determining the molecular weights of new substances. Just as those of gases were determined by their vapour densities, in accordance with the principle of Avogadro, so have those of liquids and solids been determined by this extension of the same principle to the liquid state of aggregation. All that is required is to dissolve a little of the substance in one of its known solvents, and to determine its osmotic pressure; or, if that is not practicable, to determine the rise in the boiling-point or the lowering of the freezing-point of the solvent when a certain amount of the substance is added to it. Since the same osmotic pressure is produced by the same number of molecules dissolved, whatever may be the substance dissolved, we immediately get to know the relative number of molecules contained in the new substance; and if we know its percentage composition, we at once obtain its correct chemical formula.

CHAPTER VIII

AFFINITY

CHEMICAL "affinity" is one of those terms which we have inherited from a remote antiquity, and which die hard, although superseded long ago by more precise conceptions. Not only does the word "affinity" lack precision, but it is useless and actually misleading. That "like seeks like" is by no means obvious even in the animate world, from which the term is derived. That "like seeks like" in chemistry is the reverse of the truth, as already pointed out by Boerhaave.

Misleading as the term was, the force denoted by it was investigated to great purpose by the earlier chemists, who managed to express a number of useful chemical facts in such semi-mystical language. Thus, Geoffroy in 1718 compiled a table of relative affinities for sulphuric acid in decreasing order as follows:—Fixed alkali, volatile alkali, absorptive earth, iron, copper, and silver. Taking one of the alkalies, the "fixed alkali" (soda and potash), he ascribed a decreasing affinity for it to the substances in the following list:—Sulphuric acid, nitric acid, hydrochloric acid, vinegar, sulphur, each of which expelled all those that followed it.

Boyle, the great precursor of Dalton, attributed the forces of affinity to the attraction between the small particles of which bodies were made up. Buffon mistakenly identified this attraction with gravitation. Lemery, on the other hand, conceived the combination of an acid with a base as due to the particles of the acid being sharp, and the particles of the base being porous—two properties suggested by the more obvious effect of them upon our own sense organs.

We do not now regard the molecules of an acid as having pointed projections which fit into cavities in the molecules of a base. But Lemery's idea has a grain of sense in it. Quite recently we find ourselves drifting in the same direction when studying the manner in which complex molecules are built up out of simpler ones.

The modern definition of affinity states that the affinity between two bodies capable of forming a compound is the work necessary to decompose the compound into the two original substances. Since the work actually done depends upon the amount of substance present, this must also be fixed. We cannot fix it as unit weight, since substances do not combine in equal weights. The most satisfactory way would be to define the affinity as the work necessary to break up a single molecule into its constituents. But the weight of a single molecule is even now not sufficiently well known. It is therefore agreed to measure the affinity of a certain standard number of molecules of the compound taken together, and to define their collective affinity as the affinity of the constituents of the compound.

THE GRAM-MOLECULE

This standard number is the number of atoms of hydrogen in one gram of hydrogen. Now if, instead of taking H atoms, we take an equal number of molecules of hydrochloric acid, HCl, we increase the weight in the proportion of the weight of the molecule HCl to the weight of the atom H. This ratio is known with great accuracy. It is 36·17, and is called the "molecular weight" of hydrochloric acid, being the sum of the atomic weights H = 1 and Cl = 35·17.

The standard number of molecules weigh, then, 36.17

grams instead of 1 gram. We have arrived at it by taking as many grams of the substance as the molecular weight contains units. Hence the term "gram-molecule" for the standard weight of the compound.

Instead of the "affinity" of the two constituents, it is now more usual to speak of the "heat of formation" of the compound, being the heat liberated in the formation of one gram-molecule of the compound—i.e. of as many grams of the compound as its molecular weight contains units.

We now see that the actual number of atoms of hydrogen in one gram of hydrogen does not figure in the definition, and we thus escape all uncertainty which still clings to that number. The latest determinations make it about 910,000 trillion, or $0{\cdot}91 \times 10^{24}$.

THE NATURE OF AFFINITY

Gravitation is hopelessly inadequate to account for the enormous forces at play in chemical processes. It would have to be increased more than 10^{40} times (an almost inconceivable amount) before it could rival the prodigious powers of electricity. To the latter we, therefore, turn now for an explanation of the energy of chemical combination. And not in vain; for electrical forces, such as we encounter in the simple and familiar glass rod and pith ball, are entirely adequate to the task, and when we calculate their action for atomic dimensions, the agreement between that action and the play of chemical forces is most striking.

Let us take an example. The heat of formation of pure gaseous hydrochloric acid is 22 kilogram-calories. In other words, the formation of 36·17 grams of HCl from H and Cl develops as much heat as would heat 22 kilograms of water 1° Centigrade. To compare this energy with electrical work, we must translate it into mechanical measure. The mechanical equivalent of 22 kilogram-calories is $22 \times 4{\cdot}2 \times 10^{10}$ ergs. This mechanical work, then, is derived from the attraction of 910,000 trillion chlorine atoms for the same number of hydrogen atoms. Apportioning this work among the atoms, we get—

$$\frac{22 \times 4{\cdot}2 \times 10^{10}}{0{\cdot}91 \times 10^{24}} = 1{\cdot}02 \times 10^{-12} \text{ erg}$$

for every pair of atoms combining.

That is the chemical side of the balance-sheet. Now consider the electrical side.

ELECTRIC ENERGY

When dilute hydrochloric acid is analysed by means of an electric current, hydrogen appears at the cathode and chlorine at the anode. The hydrogen ion, in becoming gaseous hydrogen, takes up one electron out of the cathode. At the anode, the chlorine ion gives up an electron and becomes gaseous or dissolved chlorine. The number of electrons thus passed through the liquid from the cathode to the anode is strictly proportional to the amount of hydrochloric acid decomposed. This is Faraday's law of electrolysis stated in the language of the electron theory, according to which an electric current through a wire consists really in the passage of electrons in the opposite direction.

The important thing for our present purpose is that whenever a hydrogen atom and a chlorine atom part company, the chlorine atom is charged negatively, and the hydrogen atom positively. The charges are equal in amount. The charge of the chlorine atom is that of one electron, and that of the hydrogen atom is the corresponding positive charge. This is easily proved by dividing the quantity of electricity passed through the electrolytic cell by the number of hydrogen or chlorine atoms liberated.

Knowing the quantity of electricity on each atom, we need only know how closely the two charges approach each other in the molecule in order to find out how much work is required to separate them.

The charge of an electron is 4×10^{-10} electrostatic units, approximately. The work required to separate an electron from an equal positive charge is

$$\frac{(4 \times 10^{-10})^2}{d}$$

where d is the distance between them. The two atomic charges can probably not get more closely together than the radius of an atom. The radius of a hydrogen atom is about 10^{-8} cm., and the radius of a chlorine atom is somewhat larger. We must therefore take it that d lies somewhere between 10^{-7} cm. and 10^{-8} cm. For the former value, the work of separating the two atoms comes out as—

$$\frac{(4 \times 10^{-10})^2}{10^{-7}} \text{ ergs.}$$

or $1{\cdot}6 \times 10^{-12}$ erg. If $d = 10^{-8}$ cm., the work is 16×10^{-12} erg. Comparing this with the chemical figure $1{\cdot}02 \times 10^{-12}$ erg., we find a remarkable agreement with the first of the two electrical values. The electrical attraction between oppositely charged atoms is therefore amply sufficient to account for the enormous thermal energy developed by chemical combination.

THERMO-CHEMICAL CONSTANTS

It is evident that we are on the straight road towards an electron theory of chemistry, so far as thermal figures are concerned. It is now only a matter of time and patience to reduce the vast mass of thermo-chemical data, notably those compiled by Julius Thomsen, of Copenhagen, to terms of electric energy. Like all sudden expansions of human faculty, it comes as something overwhelming the capacity of isolated workers. The harvest is one of magnificent promise, but unless we want to get lost in a maze of detail, some simplifying and unifying principles will have to be discovered.

It is necessary, first of all, to establish a close relation between all the reactions in which the calorimeter plays a part. There is the heat of thermal dissociation, in the first place. According to Boltzmann, one gram-molecule of iodine requires 28·5 kilogram-calories for the complete dissociation of its molecules into atoms. This means that when a molecule of iodine, consisting of two atoms, is split up, one atom takes with it an electron, depriving the other atom of it, and leaving it with a positive charge; and, in addition, that the original distance between the electron and the positive atom is about 10^{-7} cm. In nitric peroxide, $N_2O_4 = 2NO_2$, the energy required is only half as large, which means that the charges are separated by twice that distance, but in acetic acid it is midway between these two.

Then there is the heat of solution, which has been already referred to; the heat of neutralisation of acids and bases; the heat of electrolytic dissociation; the heat of liquid dissociation unaccompanied by the formation of ions; the latent heat of fusion; and the latent heat of vaporisation. These are not as yet directly available for electrical treatment, as we know too little of the actual structure of solids and liquids, and the charges of solid molecules. The heats of fusion of most organic substances range from 2·3 kgr.-calories per gram-molecule (the value for benzol) to 13·5 (the value for stearic acid). The more complex molecules show the greater heat of fusion, which suggests that a larger number of electric bonds are ruptured in fusing them than in fusing such a simple body as ice, which only requires 1·4 kgr.-calories. Some work has already been begun in tracing the relation between the volume of the atom and the melting-point, and between the effects produced by substituting one element for another in a complex molecule.

The small values of the heats of fusion, in comparison with the heats of formation, show that even after a substance has become liquefied, much energy remains to be expended upon it before the electrical forces accompanying the intimate contact of the molecules are completely neutralised.

The latent heat of vaporisation represents, roughly, the balance of this electrical energy. In some substances, such as carbon dioxide, it depends largely upon the temperature, being 3·2 kgr.-calories per gr.-mol. at – 25°C., 2·5 at 0°C., and 1·4 at 22°C. But in this case, most of the separating work is no doubt done by the heat in expanding the liquid before evaporation. Some organic liquids, such as chloral hydrate, show values as high as 21·9, but the heat of vaporisation of most organic substances is below that of water, viz. 9·6 kgr.-mol. per gram-molecule, or 532 per kilogram.

SIZE OF THE ATOM

The next task of the electrician will be to determine the manner in which the electron is associated with the atom. For as soon as we know this, we shall have a new means of determining the sizes of atoms. From the calculation of the heat of combination of H and Cl above, we have seen that the two elementary charges probably approach to within a little more than 10^{-7} cm., say $1 \cdot 6 \times 10^{-7}$ cm. Now, the charge on the chlorine atom is one electron, which has a diameter so small that it is practically a point in comparison with the hydrogen atom from which it has been captured by the chlorine atom. We therefore may know very soon exactly where we must locate the electron. As regards the positive charge of the hydrogen atom, the case is much more difficult. We are accustomed, with Sir J. J. Thomson, to look upon the positive electricity as uniformly spread over the comparatively large body of the atom. In that case, its full effect upon an electron which leaves it is not attained until it just reaches the surface of the hydrogen atom. On the other hand, we can hardly suppose the electron would be captured at all unless it were close to that surface. But once it goes outside that surface, the charge of the positive atom may be regarded as concentrated at its centre, and the distance *d* from which the electron starts is simply the radius of the hydrogen atom.

This radius, according to the above calculation, would be 16×10^{-8} cm., or about eight times the radius of the molecule of hydrogen as derived from the viscosity of hydrogen. This is a remarkable discrepancy. We have no other direct means of determining the radius of the atom; but it is not impossible that the combination of two atoms to make a molecule considerably reduces the diameter of both, and such a reduction may account for the heat liberated.

If the reasoning from electrical forces were as trustworthy as it is suggestive and alluring, we might determine the radii of atoms of most of the elements from their heats of formation when combining with "electro-negative" elements —i e. elements capable of depriving them of electrons. Taking, for instance, the chlorides of lithium, sodium, potassium, calcium, strontium, barium, zinc, and cadmium, we get the following values for $d \times 10^8$:—Li 3·5, Na 3·3, K 3·0; Ca 3·8, Sr 3·5, Ba 3·0; Zn 6·6, Cd 6·7. It is noteworthy that these values are in just the reverse order compared with the atomic volumes obtained by dividing the volume of a gram of each substance in the solid state by the number of atoms in the gram. This, however, does not invalidate the method here used. It only serves to point out another suggestive difference between the solid and liquid states of aggregation.

SHAPE OF THE ATOMS

Lemery's "pointed" molecules of acid do not seem so absurd when we deal with the mechanism of electric attraction between molecules. The carbon atom is already regarded as a tetrahedron. Nor can we see anything very extraordinary in that view, considering that the earth itself shows traces of a tetrahedral structure! A tetrahedron is that regular solid which gives the greatest surface per volume. If the surface of an atom were elastic, and its volume restricted, and the positive charge within it could expend most energy by spreading over the largest possible surface, the atom would inevitably assume the shape of a tetrahedron. The theory of gases indicates that the simpler molecules behave very much like perfectly elastic spheres. But it is nearly certain that the more complex organic molecules have very elaborate and complicated shapes, many of them being undoubtedly ring-shaped. If that is so, it may well happen that electric charges reside on some outlying portions of the rings or other structures, and when opposite charges combine, an amount of energy may be liberated which is greatly in excess of the amount liberated if the charges resided within the molecules. In the latter case, the charges would only approach to within a comparatively great distance. Again, a "pointed" molecule may actually "penetrate" into, say, a ring-shaped molecule. It may even bear an electric charge at its "point," which may combine with an opposite charge within the ring. Such cases are suggested by the various linkings of carbon atoms, their freedom, or their "steric hindrance." It is truly a wide and fascinating outlook, which may well attract new explorers into these secret recesses of Nature's workshop.

CHAPTER IX

VALENCY

In approaching the subject of valency—sometimes called atomicity, or quantivalence—we come face to face with chaos. The most cheerful view to take of it is that out of chaos some cosmos may be destined to emerge. At present everything is in a state of disintegration, or transition, or recrystallisation. The only steady light is shown by the fourfold valency of the carbon atom.

As a preliminary step towards a clearance, let us agree upon a terminology. Are we to say "quadrivalent" or "tetravalent," "quinquivalent" or "pentavalent"? We find one atom of chlorine combining with one atom of hydrogen; one atom of oxygen with two atoms of hydrogen; one atom of nitrogen with three of hydrogen; one atom of carbon with four of hydrogen. These combinations yield us HCl hydrochloric acid, H_2O water, NH_3 ammonia, and CH_4 marsh gas respectively. Hence we speak of monovalent chlorine, divalent oxygen, trivalent nitrogen, and tetravalent carbon. At least, that is how we used to do it in the older-days. But we have latterly become purists, and our sense of linguistic propriety is offended by "hybrids" consisting of a mixture of Greek and Latin roots. Even the word "scientist," though firmly rooted in the language, is rigidly excluded from the more orthodox publications as having a Latin stem and a Greek termination. Yet such "monstrosities" as "dentist" and "pianist" are admitted, and "centimetre" and "millimetre," although hybrids, are universally recognised.

However, since the Chemical Society—which, by its admirable publications, practically controls the English language of chemistry—has definitely adopted "pure" terms, we may consider the matter as settled as far as English usage is concerned. For reference, we may here quote the Greek and Latin prefixes side by side.

NUMBER.	GREEK.	LATIN.
One	Mono	Uni
Two	Di	Bi
Three	Tri	Tri
Four	Tetra	Quadri
Five	Penta	Quinqui
Six	Hexa	Sexa
Seven	Hepta	Septa
Eight	Octo	Octa
Half	Hemi	Semi
Whole	Holo	Omni
Equal	Homo	Equi
Many	Poly	Multi

We may say monatomic, dihedral, hexagon, polyglot, which are pure Greek. We may say bicarbonate and bilateral, but must no longer say binoxide or bi-symmetrical. We may be "semi"-suffocated, but we can only be "hemi"-asphyxiated, or, to put it in good plain Saxon, half choked.

CONSTANT AND MULTIPLE PROPORTION

The doctrine of valency was the inevitable outcome of the atomic theory. Possibly, its further developments may prove the undoing of that theory. Since Proust proved that two elements can combine in two or more different proportions, and thus form two or more distinct compounds, the question as to whether the elements as they exist in the compounds are really the same, or different, has always lurked in the background of the chemical consciousness. It was Dalton who first used chemical symbols to represent the genesis of new substances. But he used circles, quaintly inscribed, and therein followed the alchemists at a distance. To Berzelius we owe the more convenient modern notation. Both these eminent discoverers were forced into the use of chemical equations by their observation of the constant proportions by weight in which bodies united, and were confirmed in this practice by Gay-Lussac's discovery of constant volumes in simple numerical relation with each other.

Having arrived at what we now consider to be the correct chemical symbols, the chemical world deliberately turned its back upon the light, and continued in its retrograde policy for over half a century. Ignoring such an elementary and suggestive fact as the combination of two volumes of hydrogen with one of oxygen to form pure water, the orthodox chemistry of the early nineteenth century restricted itself to the *weights* of the combining gases, and regarded the "equivalent," or "combining weight," of oxygen as 8. The symbol HO for water was accepted in consequence of a blind prejudice in favour of Dalton's guess that the most stable compounds must consist of molecules made up of a single atom of each combining substance. This view, for which there was no experimental evidence, continued to hold the field until Kekulé, by a series of brilliant researches, firmly established the doctrine of valency (originally formulated by Edward Frankland) in organic chemistry, where ever since his time it has held undisputed sway. When an organic chemist champions the doctrine, he has before his mind the quadrivalence of carbon, the unshaken bedrock of the carbon compounds. In passing from organic to inorganic chemistry, the doctrine of valency encounters innumerable difficulties. But in Faraday's laws of electrolysis, on the one hand, and in the periodic system of the elements on the other, it receives sufficient support to entitle it to a respectful consideration.

Take these three compounds—CH_2 marsh-gas (methane), CO_2 carbon dioxide, and OH_2 water. All these can be accounted for by ascribing a single value or valency to hydrogen, a double valency to oxygen, and a fourfold valency to carbon. But, then, what about C_2H_2 acetylene, H_2O_2 hydrogen peroxide, and CO carbon monoxide? If the hydrogen peroxide is dismissed on account of its instability, and the acetylene on account of its explosive compounds, there remains the unaccountably stable monoxide of carbon. If carbon is still to be quadrivalent—and no organic chemist, except Gomberg, will hear of anything else—we must ascribe a fourfold valency to oxygen in CO, and a twofold valency to oxygen in CO_2. Other elements, notably mercury, iron, chromium, and manganese, and, indeed, practically all the elements except carbon, the "noble" gases, and the metals of the alkalies, show evidence of a variable valency.

WHAT IS AN ELEMENT?

But once we admit a variable valency, how can we identify the element possessing it? Kekulé regarded the valency of an element as absolutely definite and permanent, as definite and permanent as its atomic weight. When brought face to face with such a series as SH_2, SO_2, and SO_3, in which sulphur is bivalent, quadrivalent, and sexavalent respectively, he supposed that sulphur was really sexavalent, but that in its lower combinations some of its valencies remain unsaturated. This brings us to Helmholtz's supposition that pairs of valencies can satisfy each other. The fact that chlorine, bromine, and iodine form series of compounds which indicate 1-, 3-, 5-, and 7-fold valencies, that iron is 2-, 4-, 6-valent, and gold 1- and 3-valent, go to support this supposition. But the researches of Victor Meyer on the gaseous chlorides of iron, and of Nilsson and Pettersson on the chlorides of indium, gallium, and chromium, deprive us of even that small comfort. For the vapour densities of those compounds, by an application of the principle of Avogadro, show distinctly that $FeCl_2$ and $FeCl_3$, and similar compounds of the other metals, are capable of an independent existence. The fact that in electrolysis an element never possesses more than two different valencies may be dismissed as a peculiarity of the liquid state, or of the state of solution. But in taking all states of aggregation into account, we must face the fact that certain elements may possess seven or eight different valencies.

We must next make up our minds whether, under the circumstances, we shall retain valency as one of the characteristics of an element. Before the days of radioactivity, such a question would have been answered in the negative without the slightest hesitation. But since the possibility is now admitted of one element being converted into another by the loss of certain electrically charged portions of its atom, we must ask ourselves seriously whether a similar process, occurring in the conversion, say, of a ferric salt into a ferrous salt, changes the iron into something which is not iron, or vice versa. The fact that, by certain processes of analysis, we can always reduce the "iron" to a certain standard condition does not decide the matter in favour of the permanent element iron. It simply begs the question. When mercuric salts are dissolved in water, each mercury atom loses two electrons. In mercurous salts, each mercury atom loses one electron. If we encountered two such bodies in a process of radioactive disintegration, we should say that mercuric mercury was formed from mercurous mercury by the loss of one electron per atom. Probably, we should denote the two "elementary" substances by HgA and HgB. The circumstance that, unlike the cases of radium and thorium, the conversion of one mercury element into another is controllable and reversible, does not cancel the analogy. It only serves to add an intense practical interest to the current efforts at controlling the spontaneous processes of radioactive change.

VALENCY AND VOLUME

The most hopeful line of advance in the matter of valency has lately been made by connecting it with the volume of the atom. This volume is arrived at along two independent lines, which yield concordant results whenever they can be got to meet. The simplest way is to divide the atomic weight of a substance by its specific gravity in the solid state. The result is a figure proportional to the volume occupied by each of the atoms in "contact." The other way is based, as already explained, upon the kinetic theory of gases.

Now, it is found, as a general rule, that in the same group of elements the tendency to lose electrons (i.e. to become "electropositive") is in direct proportion to the atomic volume. Thus, in the alkaline series of elements, lithium is the least electropositive, and cæsium the most. In the bismuth series we have nitrogen, an electropositive element, at one end, and bismuth, an electronegative element, at the other. Again, in the non-metallic halogens, where the atomic volume also increases with the atomic weight, the most electronegative element is the lightest, fluorine, and the least electronegative is the heaviest, iodine.

In this connection, it is interesting to observe that when two positively electrified spheres are in contact, and an electron is placed at their point of contact, the electron will, on separating the spheres, remain attached to the smaller sphere, since the positive charge, concentrated on the smaller sphere, is practically at a smaller distance from the electron, and, therefore, exerts a more powerful attraction if the two positive charges are equal.

REFRACTIVITY

Another line of investigation which considerably stengthens this argument is that of atomic refraction. Traube showed, two years ago, that the contribution of each atom to the refractive index of the substance is directly proportional to its volume, and this, again, is proportional to its detachable electrons or valency electrons. In fact, the electrons which produce valency, and make chemical combination possible, are identical with the electrons which produce the dispersion of light, and are responsible for colour effects. Traube determined the refractivities of a large number of organic compounds, and found that the individual refractivities of the atoms of carbon, nitrogen, oxygen, and hydrogen had the ratio 4: 3: 2: 1, which is also that of their lowest, or "fundamental," valencies. Given the refractive index of a substance and its molecular weight, it is easy to arrive at its molecular refractivity by dividing the first number by the second. The molecular refractivity is proportional to the total valencies, links, or bonds within the molecule. To determine the valency of a new element, therefore, it suffices to substitute an atom of it for a known element in a known organic compound, and to determine the refractive index of the new compound.

ATOMICITY

Alluring as these new avenues of research are, they do not reach the root difficulty. For the relation between valency and volume is not a simple one. The halogens are all electronegative, and yet they have large atomic volumes. It is only in the same group of elements that the relation holds good. Again, the combination of atoms of the same gas into diatomic or triatomic molecules is left entirely unexplained. The term "atomicity," sometimes used instead of valency, should be restricted to the number of atoms in the molecules of elementary substances. Mercury and cadmium vapours, and even liquid mercury are monatomic, and so are the "noble" gases recently discovered in the atmosphere. But hydrogen, oxygen, and nitrogen are diatomic gases. And as the formation of their molecules is attended with the evolution of an amount of heat suggesting electrostatic forces, we must conclude that single atoms of these gases are positively and negatively charged in about equal numbers, in the gaseous state at all events. Must we not, therefore, consider that "nascent" hydrogen really consists of two forms of hydrogen, especially as the two ions can be actually separated by an electrostatic field?

ELECTROLYTES

When a salt is dissolved in water it is dissociated into ions. Those which lose electrons go to the cathode; those which gain them, to the anode. If they neither lose nor gain electrons, they do not obey the electric forces, and the substance is not electrolysed. Carbon does not exist as an ion in any known liquid. Yet it has four valencies. It follows that two of these valencies must be positive, and two negative. As the carbon atom is most likely a tetrahedron, we must imagine two electrons located at two points, and two positive centres located at two points in a line at right angles to the line joining the electrons. Such an arrangement is full of chemical and optical possibilities, and we shall see that the carbon atom knows how to avail itself of them.

CHAPTER X

CHEMISTRY AND ELECTRICITY

IF the electron theory of electricity and magnetism is barely ten years old, the theory of electrolytic dissociation which now holds the field has seen about twice that number of years. Less far-reaching than the former, because confined to conducting liquids, it yet covers an immense array of facts. But then, on the other hand, it is contradicted by a very formidable array of other facts. That it holds the field is due, not to its uniform success in explaining the behaviour of electrolytes, but to the vivid light it throws on many phenomena of the liquid state, to the suggestive manner in which it links itself with modern electrical theory, and, above all, to the genius, industry, and persuasiveness of its founders.

Among these, Arrhenius holds the chief place. Ostwald, Kohlrausch, Nernst, and Van't Hoff must be reckoned as prominent authorities on solution in general who have utilised and supported the conceptions of Arrhenius, while Krönig, Paul, Kahlenberg, Loeb, Bredig, Clark, and numerous other electro-chemists have successfully applied the theory of electrolytic dissociation to various new lines of inquiry.

If, in the end, the theory of electrolytic dissociation should turn out to be false, it will prove once more what immense services to science even a mistaken theory can render, provided it links together a number of facts which were disconnected. At present, in spite of severe and continuous criticism, the theory is holding its own. It is like a Government living under a daily threat of revolution, which maintains itself in power by sheer consistency and the dissensions of its opponents. And that Government has a fine record of "beneficial legislation" wherewith to face public opinion. If its Armageddon ever comes, the struggle will be worth living to see.

THE NATURE OF ELECTROLYSIS

It was in 1887 that the great Swedish electro-chemist, Svante Arrhenius (worthy successor to Berzelius) propounded his theory of electrolytic dissociation in the newly established "Zeitschrift für Physikalische Chemie." In doing so, he utilised the "by-products" of the osmotic theory in the shape of consistent irregularities, all of which could be brought into touch with each other by putting the liquids showing these irregularities into a class by themselves. They were found to include the most important inorganic acids, bases, and salts, those bodies which played the most practical parts in chemical analysis and chemical separations. Their irregularities of behaviour, whether in the matter of vapour pressure, osmotic pressure, freezing-point, or boiling-point, all took the same direction. They indicated an excess of molecules beyond their theoretical number. The great achievement of Arrhenius was to connect this behaviour with the old electrolytic hypothesis of Grotthus, and with its later developments due to Clausius and Kohlrausch.

Let us briefly survey the line of argument. Grotthus observed that however far apart the electrodes are placed, the products of electrolysis appear simultaneously at both electrodes. This means that they cannot be derived from the same set of molecules. He therefore imagined a chain of molecules (say, of HCl), stretching across between the electrodes under the pull of the electric force. This chain, originally of the form—

$$- \mathrm{HCl\ HCl\ HCl\ HCl} +$$

becomes, by liberation of one atom of each substance—

$$- \mathrm{H\ ClH\ ClH\ ClH\ Cl} + .$$

The electric force then turns round the ClH molecules into the HCl position, while the liberated H and Cl appear at the electrodes. The new chain—

$$- \mathrm{HCl\ HCl\ HCl} +$$

undergoes the same double process, until all the hydrochloric acid is decomposed.

THE WANDERING OF THE IONS

So far the hypothesis of Grotthus, put forward as long ago as 1805. It accounted for all the facts for half a century; but it suggested an important question, which has hardly yet been finally solved. In what state are the atoms H and Cl in the interior of the liquid during their exchange from one molecule to the next? Obviously, they must be uncombined, at least for a very short interval. Faraday assumed some such temporary freedom, and chemists generally found no difficulty in agreeing with him, more especially as something of the kind had to be assumed in every chemical reaction. The next question to be asked was whether the short distance from one molecule to the next was traversed by both atoms with the same speed. For if it were not, there would be a general displacement in the direction of the faster atom. This question was asked and answered by Hittorf, who, in a series of painstaking and ingenious experiments, proved that different ions may have very different velocities under the same electric force. He carefully determined the shifting of the electrolyte towards one of the electrodes by measuring the concentration at the anode and cathode respectively after the current had passed for a given time. The percentage losses of concentration at the electrodes are inversely proportional to the speeds of the ions liberated there. Thus, in the case of hydrochloric acid, the disappearance of the electrolyte is most rapid at the anode, since the hydrogen wanders away from it at a greater speed than that of the chlorine wandering towards it. Hittorf called the relative speeds of the ions, as measured by the concentrations, "transfer numbers" (in German: Überführungszahlen), a word chosen more for its non-committal character than for its appropriateness. The transfer number of an ion may be defined as "the proportion of the total current which it conveys." This is the simplest definition, and is quite in accordance with modern views; for the current through an electrolyte *is* the streaming of the ions, and nothing else. As a rule, it consists of a stream of positive ions towards the cathode *plus* a stream of negative ions towards the anode. These streams are not necessarily equal. We could imagine the chlorine ions to be so large as to be practically motionless. The current through the hydrochloric acid solution would only be reduced some 17 per cent thereby. In fact, in a current which passes through HCl solution, 82·5 per cent of the current is transferred by the H ions, and only 17·5 per cent by the Cl ions. The "transfer numbers" of H and Cl are therefore 0·825 and 0·175 respectively.

In a wire we have an extreme case of one-sided transference; for all the current is carried by the electrons, whose "transfer number" is therefore unity. No current is carried by the metallic atoms, and their transfer number is therefore zero in the solid state.

If there are two kinds of ions in a solution, and the transfer number of one of them is n, that of the other is $1-n$. Since the total amount of substance decomposed is, according to Faraday's law, proportional to the quantity of electricity which has passed through the cell, the total loss of concentration measures that quantity, and the proportions due to the two ions are measured by the relative losses at the opposite electrodes. If n is the proportion conveyed by the anion to the anode, and $1-n$ the proportion conveyed by the cation to the cathode, and l_a and l_c are the losses of concentration at the anode and cathode respectively, we have the equation:—

$$\frac{n}{1-n}=\frac{l_a}{l_c}$$

$$\text{or } n=\frac{l_a}{l_c+l_a}$$

ACTUAL VELOCITIES OF THE IONS

The above equations give us only relative velocities of the ions. The absolute velocities depend upon the driving force on the ions, and the resistance encountered by them. Now, the driving force is nothing but the electric force due to the charges on the electrodes—in other words, the effect of the "field" within the liquid upon the charged ions. The resistance is the viscous resistance of the same liquid. Knowing the resulting velocity, we have valuable data for judging of the constitution and structure of the ions.

Now, this velocity is not at all difficult to determine. Imagine a cubic cm. of dilute copper sulphate, with two opposite faces consisting of copper plates at a difference of potential of one volt. This gives a "potential-gradient" of one volt per cm. Let the resistance of the cube be 100 ohms. Then the current will be $^1/_{100}$ ampère. This current will transfer 0·0000326 grams of copper every second from the anode towards the cathode, without altering the strength of the solution. The whole cubic cm. of solution contains this quantity, say 1000 times. Hence the whole of the dissolved copper contained at a given moment in the solution will have been deposited after the lapse of 1000 seconds. This means that the last copper ions deposited will have travelled one cm. in 1000 seconds. This, then, will be the velocity of the ions of copper under the force of a potential gradient of one volt per cm.

A large number of such velocities have been measured in this manner. We may quote a few:—

CATIONS.		ANIONS.	
Potassium	0·000669	Chlorine	0·000677
Sodium	0·000450	NO_3	0·000640
Lithium	0·000346	OH	0·001802
Hydrogen	0·003294	cm. per sec.	

It will be seen at once that hydrogen and hydroxyl (HO) have by far the greatest mobilities, that of the latter being about three times as great as that of any other ion except hydrogen. It is also clear that there is no connection between atomic or molecular weight and mobility. In fact, we cannot here have to deal simply with atoms or molecules disseminated freely through the water.

HYDRATION OF THE IONS

It is here that we plunge into the great controversy which still rages about electrolytic conduction. It concerns the structure of the ions. Chlorine ions and the negative ions of perchloric acid, ClO_4, have the same mobility. The light lithium atom has only half the mobility of the heavy thallium atom, and only one-tenth of that of the still lighter hydrogen atom. The situation bristles with anomalies.

Evidently we must conclude that the ions are combined to some extent with the solvent, and that if any ions are quite free, they can only be those of H and HO. This supposition is greatly strengthened by an actual calculation of the resistance offered by the water to individual ions. We know from the theory of gases what kind of sizes the atoms most probably possess. We also know the electric driving force. With this knowledge we can determine the resistance which they would encounter in moving through the water, just as we can determine the resistance experienced by a ship. When this is done, it turns out to be just about the same as the resistance offered by the water-molecules to each other's motion. In fact, it is the ordinary viscous resistance familiar to us in experiments on capillarity. Hence the ions are all hydrated, and embedded in rings, chains, or other groupings of water-molecules.

From a study of the changes of volume undergone by liquids when mixed together, Holmes has recently arrived at the astonishing conclusion that neither a substance in aqueous solution nor water itself is "hydrated." It has been asserted, in fact, that there is no way of proving the hydration of ions except by pointing out how easy it would be to explain ionic mobilities if it existed!

On the other hand, Armstrong and his disciples have devised some ingenious experiments tending to place such hydration clearly in evidence. One of these is to add a few drops of alcohol to water, and determine the solubility of salts in it. Since alcohol itself takes up water, it is to be expected that sodium chloride will have less water with which to hydrate its ions. As a matter of fact, it is less soluble in alcoholic water than in pure water. A more convincing experiment is that of Jones and Uhler, who have studied the absorption spectra of aqueous solutions of strongly coloured salts, such as those of copper and cobalt. When desiccating agents, such as calcium chloride or aluminium chloride, are added to the coloured solutions, the effect on the spectroscope is the same as if the original solution were concentrated. The drying-salt deprives the copper or cobalt salt of some of its water of hydration.

RECENT DEVELOPMENTS

We have already briefly referred to the great array of confirmations which the electric dissociation theory has succeeded in rallying round itself. These are still increasing. Ever since Arrhenius perceived that all the "irregular" solutions conducted the electric current, the same regular irregularities have been found in all sorts of out-of-the-way properties. In addition to the vapour-pressure, boiling-point, freezing-point, and osmotic pressure, we now have evidence of dissociated and independent ions in absorption spectra (Ostwald), densities of liquids (Valson), molecular refractions (Le Blanc), and in the molecular rotation of the plane of polarisation (Oudemans). We have also parallel anomalies in compressibility, capillarity, and viscosity, as well as in the Faraday effect, and also, it is alleged, in molecular magnetism. It has even been proved that the only effective parts of poisons are their dissociated ions, and it does not matter which of their compounds gives rise to the ions.

And, lastly, take a most significant fact, sufficient by itself to establish the theory.

The heat of neutralisation of all dilute acid and basis is *equal to the heat of formation of water.* When an acid like HCl and a base like NaHO are both contained in a very dilute solution, in which they are completely split up into H, Cl, Na, and HO ions, only the H and HO ions combine to form water, and no other combination takes place. The same is true of all acids and all bases in dilute solution. This clearly indicates the splitting up of both into independent ions.

Facts like these are difficult to explain away, and it is facts like these which have put the theory of Arrhenius into the proud position it holds to-day. When first propounded, it flew in the face of all chemical opinion. Nobody who had witnessed the violent action of metallic sodium on water could imagine that atoms of pure sodium could exist in water except in some molecular combination. Yet to-day we believe not only that metallic sodium exists in sea-water, free from the chlorine to which it was originally attached, but that it protects itself from combination by gathering about itself a mantle of that very substance with which we have seen it combine with almost explosive violence.

CHAPTER XI

CHEMICAL ANALYSIS

"THE number of properties belonging to any particular substance is infinite." This statement by the greatest living German chemist, Wilhelm Ostwald, may be surprising at first sight; but it is strictly true. We cannot assign a limit to the number of properties of a substance. For these properties are measured by the number of tests which we can apply. We can do a large number of different things to a given substance, and can apply those processes either separately or together. Every day we are inventing new tests. Yesterday we compressed or stretched, heated or cooled, watered or dried a substance. To-day we determine its behaviour in the electric furnace, or in the vacuum tube, or in a stream of radium emanation. To-morrow we may, perhaps, take it through a cycle of alchemical transmutations, or apply it to those vast intra-atomic forces whose very existence was unsuspected ten or twelve years ago.

But here a logical difficulty arises. If every substance has an infinite number of properties, how can we ever identify it? We cannot determine *all* its properties, and it may thus happen that it agrees with another substance in, say, a thousand properties, and yet is perfectly distinct and separable in the one thousand and first. There is no escape from this dilemma, and no element, however apparently simple, is quite free from the risk of being split into two or more distinct constituents.

The matter for surprise is not the large number of different substances already recognised. The surprise is rather that the number of substances, as of living species, is limited. The number of recognisable properties being infinite, the number of substances theoretically possible is an infinity of a higher order. But in the lottery of existence there are vastly more blanks than prizes. The combinations of properties which "survive" are remarkably few, and it is this peculiarity which enables us to recognise and identify a chemical species with the same facility and dispatch as we identify a species in botany or zoology.

This survival of the few has given rise to an unconscious rule which we apply to chemical analysis. We identify a substance by only a few of its properties. We find its density, its fusing-point, its boiling-point, its spectrum, its behaviour in the presence of a few discriminating reagents, its atomic or molecular weight. When all these agree with those of a known substance, we identify the two substances without further parley, and take the risk of any discrepancy which may be discovered at some future time.

We even go further than this. We identify two substances which do *not* agree in a number of properties. We identify solid sulphur with liquid sulphur and with sulphur vapour; in the solid state, we identify rhombic sulphur with its monoclinic "allotropic" form. We identify all these different bodies with the sulphur mysteriously embalmed in oil of vitriol and copper sulphate and galena. We identify diamond, and graphite, and amorphous carbon because, forsooth, they all yield the same substance on burning in pure oxygen. In the gaseous state, we identify triatomic ozone with diatomic oxygen and monatomic "nascent" oxygen. We do all this because, given one modification, we find ourselves able to convert it into any of the others, or because we believe that our ability to do so is only a question of time.

When we cannot obtain a substance as the sole result of the combination of two or more other substances, we call it an "element." The elementary nature of gold was found out in this manner by patient endeavour stretching over weary centuries, at the great cost of the alchemists and their deluded patrons. The strain of that long endeavour, and the bitterness of its final failure, have left an indelible mark on the human consciousness. The elements have proved the stronger, and their prestige is overwhelming. Only quite recently have the dreams of the alchemists been revived, when the phenomena of radioactivity revealed the secret of the mighty forces which keep the elements what they are.

MECHANICAL SEPARATION

If the existence of the irreducible and immutable elements is a fact brought home to us by a long series of failures, our belief in the temporary and changeable nature of chemical compounds is the triumphant conclusion of a career of successes. These successes have convinced us that what we can build up we can also destroy. We cannot as yet control the forces which hold the atom together. But we can, and do, control all forces short of those, and our province is surely a vast one. When Prometheus brought fire down to the earth, he extended our powers from the molar to the molecular region. He enabled us to utilise the forces at play between the atoms, and to interfere effectively in processes which are quite hidden from our sight, with all its modern extensions. The powers of heat enable us to meet the atoms on their own ground. By imparting heat to a compound, we are able to counteract the powerful electric forces between the atoms, and to tear them from their molecular combinations.

Once that is done, the separation of two substances becomes a purely mechanical operation. All we require is a surface of separation to which we may apply the necessary mechanical force. As Ostwald puts it: "The separation of substances is always a mechanical separation; a so-called chemical separation consists in transforming the substances in question, by chemical means, into others which can be separated mechanically."

The three states of aggregation furnish us with six distinct problems of separation. In a mixture of two substances, both may be solid, or liquid, or gaseous; that gives three cases. Besides these, we have the separation (usually easier) of bodies in different states of aggregation: solid and liquid, solid and gas, liquid and gas.

The separation of solids from solids is a problem solved in various ways in the human world from its earliest times, and even in the animal world. The wedge or knife, with its natural counterparts of tooth and claw, are used to produce surfaces of separation to which molar forces can be applied. The hand, the rake, and the sieve are instruments for applying these molar forces. But these only serve to separate solids differing in size or structure. In chemical substances, size and structure are only secondary properties. Density is a much more intrinsic property, and is of great chemical significance. It is, therefore, utilised in the separation of solids, as in the washing of gold ore, and the separation of minerals by heavy liquids of graduated density, such as aqueous solutions of barium-mercury iodide or cadmium borotungstate; methylene iodide or acetylene tetrabromide for substances soluble in water; or fused solids for substances which can be safely heated. But the cold liquids cannot be made heavier than three times the density of water, and a continuous gradation of liquids from half to thirteen times the density of water would be a great boon. Why should there be no means of "diluting" mercury to one-quarter of its density? The separation of solids by magnetic force, as in certain iron ores, and their electrical separation based on differences of specific inductive capacity cannot as yet claim to be out of the experimental stage.

The separation of liquids and gases from each other is, with our present means, very imperfect and unsatisfactory. Here again the difficulty lies in securing a separating surface. When two liquids neither mix nor combine, and have different densities, it is comparatively easy to draw one of them off, especially when the surface between them is reduced to a small meniscus. But such cases are rare, and in gases they are impossible. Gases are only very imperfectly separated by diffusion. It is true that hydrogen molecules move, on the average, four times as fast as oxygen molecules; but that applies only to the average, and the vanguard of the oxygen army is always ahead of the stragglers among the hydrogen molecules. The only effective "filter" for hydrogen—and the only gas-filter known, so far—is red-hot platinum or palladium, through which hydrogen passes with comparative ease. Absorption by charcoal or iron is sometimes very effective, as proved by Bordas in the case of helium.

In this connection, it is well to remember Sir William Ramsay's caution concerning the possibility of discovering gases. In practice, we cannot discover gases capable of passing through glass. Glass or silica vessels are used in gas analysis, and even if they could be avoided, we could not apply the most useful of all gas tests—the spectroscopic one—without enclosing the concentrated gas in some transparent vessel. We do not know of any gases which can pass through glass, or through cold glass, at all events. But if any such existed, it would be impossible to discover them with our present means. What a vista of future possibilities!

FILTRATION

Gases and vapours are easily separated from solids and liquids, especially if they turn solid (sublimation) or liquid (distillation) on reaching a cooler region. But by far the most usual and useful method of separation is by filtration.

The analyst's apparatus consists largely of glass funnels, filter-paper, and apparatus for weighing, burning, or otherwise dealing with filter-paper and precipitates. Modern improvements all tend to the more rapid and complete separation of the precipitate from the filtrate. Thus we have contrivances for heating and digesting the precipitate in the solution, which increases the size of the larger crystals at the expense of the smaller ones, and thus renders the precipitate less liable to clog the paper. For the same purpose, we have reagents for coagulating the very troublesome colloid precipitates, which are really very fine suspensions. Filter-papers are produced of all degrees of fineness and strength, and the amount of ash left after igniting one of them is often less than a milligram. The rate of filtration is increased by mounting the funnel in the stopper of a jar which is exhausted, so as to make the atmosphere press the filtrate through the pores. The vacuum is produced by a pump, such as Körting's water-jet pump, which is worked by simply turning on a jet of water having a head of 15 ft.

With all these improvements, we cannot yet be sure of attaining a complete separation. For the solution is more concentrated near a solid surface than in the body of the liquid. As a consequence, the solution tends to cling about the particles of the precipitate, and clings the more closely the smaller they are. It also remains in the pores of the filter-paper. This phenomenon is known as "adsorption," and its laws are still very obscure. The best remedy lies in a judicious series of washings, following a rule of "little and often." No method has yet been devised which will wash out a copper filtrate so that the precipitate no longer reacts to Delépine's copper test. This test consists of a brown coloration produced by a solution of a dialkyldithiocarbamate, and is capable, it is said, of discovering one part in a million.

THE CENTRIFUGE

Many attempts have been made to eliminate the filter-paper altogether. An interesting device of this kind is the apparatus quite recently devised by H. G. Parker. A flask-shaped tube open at both ends is filled with the solution, which is precipitated by a suitable reagent. The neck of the flask fits into a weighed platinum crucible by means of a firm, watertight joint, made by a short section of rubber tubing, which is held between the outside of the neck and the inside of the crucible. The flask, with the crucible, is then placed in the jacket of a specially constructed centrifuge, and the space between is filled with water; the hydrostatic pressure being the same inside and outside the flask, there is no tendency to leak. A few minutes' rotation at a speed of 1500 to 1800 revolutions per minute causes the precipitate to collect in the crucible. The flask is removed from the jacket, the water is drawn off by means of an ordinary siphon bottle, and the precipitate is washed three times with a very little water, each time repeating the process. Finally, the crucible is detached from the flask, dried, ignited if necessary, and weighed.

It is possible that filter-paper may be got rid of altogether. It has been alleged that even the purest filter-paper gets contaminated by oxides of nitrogen, which are formed by the combination of atmospheric oxygen and nitrogen in its pores. It is difficult to see how this is ever to be avoided. Asbestos appears to have no such action, and filters of asbestos fibre are being more extensively used, although their range of application is limited.

INDICATORS

In qualitative analysis, all that is required, as a rule, is that we should know five or six properties of a substance in order to determine its composition. We make a solution of it, and add to it a little hydrochloric acid, sulphuretted hydrogen, ammonia, ammonium chloride, and ammonium carbonate, filtering whenever a precipitate appears, and testing the precipitate further. This process discriminates between certain groups of metallic elements, or, rather, of metallic ions. Some of them are precipitated as chlorides, others as sulphides, hydrates, or carbonates. The rate of precipitation is governed by the Law of Mass Action, discovered by Guldberg and Waage, according to which the reaction is proportional to the product of the concentrations of the two bodies reacting on each other. The modern theory of dissociation has proved that all chemical reactions are accompanied by their opposites, in accordance with the law of mass action. Thus, carbonic acid is capable of slowly decomposing barium sulphate, though sulphuric acid rapidly decomposes barium carbonate. The removal of the newly formed substance by precipitation has the effect of making the reversed action exceedingly slow, and practically negligible.

But a ready means of estimating quantities required for a reaction is offered by the so-called "indicators," usually substances changed in colour as soon as a certain state of equilibrium is reached. The best-known indicator is litmus tincture or lacmoid, which is coloured blue in an alkaline solution and red in an acid solution; or, rather, the blue colour is produced by OH ions, and the red by H ions. Phenolphthalein is another indicator of comparatively recent discovery. "Resorubin," obtained from resorcin, is ordinarily violet, but is turned blue by alkalies and yellow by acids. These indicators serve the purpose of the pointer or needle on a scale, by indicating the stage at which the quantity of a reagent used just suffices to produce a certain reaction. Much of the recent progress of quantitative analysis is due to the discovery of special indicators for special cases.

UNIV. OF CALIFORNIA

ELECTRIC ANALYSIS

Electro-chemical methods of analysis have been developed with the advance of electro-chemistry. They offer the advantage of a strict control of the quantity of energy consumed, and also a certain facility of manipulation. Rotating electrodes have been extensively adopted where rapidity is essential; but the credit of their first adoption has given rise to a lively controversy.

For the most delicate analytical work, dealing with quantities of less than a milligramme, the usual chemical tests have to give way before optical and electrical methods. The spectroscope is still unrivalled for delicacy, but is seriously threatened by some new methods used in radioactivity. By one of these—that of gaseous ionisation—Rutherford has been able to identify and discover the action of a single atom, and he has watched the flash of light produced by its impact upon a luminescent screen.

THE MICRO-BALANCE

Meanwhile the principle of the common balance has received a startling extension in the hands of B. D. Steele and Kerr Grant,* who made the beam of a framework of thin quartz rods, weighing together less than half a gram. Instead of weights, there is a single counterpoise consisting of a small flask filled with air. The whole is put into a brass box tinned inside and made air-tight with a cement consisting of 95 per cent shellac and 5 per cent oil of cloves. The pressure of the air in the box regulates the buoyancy of the counterpoise, so that there is no necessity to change the weights. The position of the beam is read by means of a mirror, scale, and telescope. The balance is capable of discovering differences of weight down to four millionths of a milligram.

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* See *Proceedings of the Royal Society*, A, 82, p. 580, 1910.

One such balance is in use in an underground room in University College, London. It is the balance with which Ramsay and Gray determined the weight of a tenth of a cubic millimetre of the emanation of radium.

This new balance brings us down to an aggregate of a million million atoms as the smallest chemical aggregate which can be "manipulated" in its entirety. Any operations on a scale more minute than this call for statistical methods of inquiry.

CHAPTER XII

CRYSTALLISATION

The science of crystals has grown up along independent lines of its own; but crystallography has not altogether escaped the strenuous efforts towards the unification of the sciences made during the last generation. When this unification is made to include the phenomena of crystallisation, we may expect a rapid advance all along the line.

The present state of things resembles that epoch in accurate surveying at which the trigonometrical surveys of France and Great Britain had both been completed, but had not yet been connected with each other. That was accomplished by taking two points on each coast and making them apices of triangles on cross-channel base-lines.

Crystallography, as a science, is built up on geometrical and optical principles, and is therefore peculiarly open to mathematical treatment. It is also capable of extreme development and elaboration, having the numberless permutations of configuration and movement for its province. It is, therefore, not surprising that crystallography should have advanced rapidly along its own lines, without paying much heed to the laborious and sometimes erratic progress of its sister sciences. It was left free to accumulate its own data, and to catalogue them on its own principles. Whenever an atomic theory of crystallisation is successfully attempted, the material for study and adaptation will be ready to hand, and will be practically inexhaustible.

It was Romé de l'Isle who first brought order into the bewildering array of natural crystals by showing how complex forms could be derived from simpler ones by cutting off their corners by means of planes inclined at certain angles. Such a process was, no doubt, suggested by the cutting of gems to give greater brilliancy to the light reflected by them—a purely empirical practice, unconnected with rational crystallography. The recognition that the extent and shape of crystalline surfaces are of little moment in comparison with the angles between the surfaces was one of those generalisations which distinguish a science from a superficial popular judgment. It entered upon its next stage when R. J. Haüy showed that a large number of crystals possess natural planes of cleavage, and that the ultimate kernel arrived at by such cleavage is always the same in the same substance. He showed how crystals could be built up from cube-shaped bricks, arranged in equal or tapering layers, and having steps in simple ratios, such as 2 : 1 or 3 : 2. But this view could not be consistently applied to crystals having no distinct cleavage, and it was not till C. S. Weiss discovered the Law of Rational Indices that a sound geometrical basis was established for the new science.

RATIONAL INDICES

If the corner of a cube is cut off by a plane surface, the amount cut off each edge, reckoning from the corner, depends upon the inclination of the surface. In actual crystals it often happens that two differently inclined surfaces cut the same corner. But then it is always found that the two lengths cut off each edge have an exceedingly simple numerical relation to each other. *The ratio is always a whole number*, and a small number, which never exceeds 6. If the plane is parallel to one of the cube surfaces, the amounts "cut off" the edges of that surface are, of course, infinite. But it is convenient to include that case also, for reasons of notation. For the law of rational indices enables us to specify any cutting plane in a simple manner. We could specify it by stating the comparative amounts cut off each edge; but it is more convenient to take the reciprocals of those amounts, and to write the figures side by side. Thus, the symbol 112 would represent a surface which cuts off equal lengths along two edges and half that length along the remaining edge. The symbol 100 indicates a surface which cuts one edge, and is parallel to the uncut surface. For the reciprocal of an infinite quantity is zero. The three original edges are not necessarily rectangular, but vary from one system of crystallisation to another. This notation was proposed by Whewell in 1825, and worked out by Grassmann, Frankenheim, Gauss, and W. H. Miller.

The law of rational indices may be derived from a law concerning " zones of surfaces," or sets of surfaces which all intersect in parallel lines. But it is really an exact expression of Haüy's cruder conception based upon cleavages. It shows that crystals must possess something resembling a bricklike structure, in which each part is geometrically similar to every other, and can be made to coincide with it by a movement of translation or rotation.

SPACE-LATTICES

The recognition of this fundamental fact gave a new zest and a new inducement to the search for a geometrical interpretation of the observed regularities. In 1850, Bravais made an exhaustive inquiry into the various ways in which small identical regular bodies can be distributed uniformly throughout unlimited space, so that each is surrounded in the same manner by its neighbours, and their axes of symmetry point in the same direction. Such an arrangement would mean that if the centres of any two of the bricks are joined by a straight line, and the whole assemblage is given a motion of translation along that line, there will, in the end, be a perfect coincidence of the bricks.

The number of such lines of translation is obviously given by the number of bricks adjoining any given brick; but as the bricks are all similarly placed, each line can be indefinitely prolonged, and will always pass through further centres of bricks. The total assemblage of such lines is called a "space-lattice." The number of distinct sets of lines in a space-lattice is half the number of bricks adjoining a given brick, since the same line passes in two opposite directions, and so cuts two bricks.

Bravais showed that fourteen kinds of such space-lattices exist, and that they correspond in their symmetry with the seven large crystal systems. The movements of translation which end in a coincidence are called "coincidence movements." These may not only be translational, but also rotational. A cube or an octahedron may be rotated about three different axes, and will coincide with itself after each turn of 90°. Any large regular assemblage consisting of them may be similarly rotated into coincidence. One complete turn gives four such coincidences, and, therefore, the cube and the octahedron are said to possess a fourfold symmetry about three rectangular axes.

UNSYMMETRICAL UNITS

When the constituent "bricks" are no longer necessarily symmetrical (i.e. having one half equal to the mirror-image of the other half), the number of possible space-lattices is greatly extended. Sohncke proved in 1876 that no less than sixty-five types of homogeneous structure may then be distinguished. But since his time, a further step has been taken, by allowing two types of similar arrangements of neighbouring molecules, one of them being the mirror-image of the other. This brings the total number of possible structures up to 230. This, however, represents the utmost limit of complexity. No further privileges can be granted. Any further concessions would make the crystal an assemblage of heterogeneous parts, like most solid metals. Every known crystal, and every crystal which may yet become known, must belong to one or other of these 230 types.

MOLECULAR DISTANCE RATIOS

So much of the ground being cleared, we may enter upon the same questions from the chemical as opposed to the purely geometrical point of view. In doing so, we must pass from the imaginary "brick" to the actual chemical unit, the molecule. And here we enter a most fascinating field of research, with a distant view of the bridge which is to unite crystallography with general chemical and physical theory.

In endeavouring to determine the actual arrangement of molecules in the crystal, and atoms in the molecule, it is safest to proceed by slight changes in the first instance. The isomorphous crystals, which have the same general shape, with, perhaps, a slight difference in the lengths of axes, offer the best point of attack. These axes are nothing but the lines joining the centres of molecules in three independent directions. If, therefore, we take a series of substances of similar structure and of nearly equal composition, we may find what difference is produced by substituting an atom of one substance for that of another.

This is what has been done most assiduously and successfully during the last twenty years by Dr. A. E. H. Tutton. The result has been that it is now possible to indicate definitely to which of the 230 possible types any given crystal belongs. Not only that, but it is even possible to indicate with great probability the actual arrangement of the atoms in the molecule.

Take, as an example, the sulphates and selenates of the three related elements—potassium, rubidium, and cæsium. In passing from the sulphate of one metal to that of the next, the greatest change occurs in the vertical axis. The same thing happens in the selenates. But in passing from the sulphate to the corresponding selenate, the change is in the opposite direction, being greatest in the two horizontal axes. From this result, Tutton concludes that the molecules of the alkali sulphates and selenates are so disposed in the crystal structures that one atom of sulphur or selenium lies between two of the alkali metals, and that all three are extended in the direction of the vertical axis.

It is Tutton's great achievement to have raised crystallography, and more particularly goniometry, to the front rank of exact sciences. His measurements of angles cover four places of decimals, and are of the same order of accuracy as modern determinations of atomic weights. He has shown, moreover, that in a closely related group of elements such as that of the alkali metals (including ammonium), all the ascertainable properties—morphological, optical, thermal, and physical—are functions of the atomic weights of the elements. Such closely related groups of isomorphous elements he proposes to call "eutropic" series. They must be distinguished from the "morphotropic" series in which the substitution of one element or constituent for another changes a crystal into one of an altogether different system, as, for instance, cubic ammonium iodide, NH_4I, into tetragonal methyl-ammonium iodide, NMe_4I, or orthorhombic propyl-ammonium iodide, NPr_4I.

COMPRESSED SPHERES

We are now prepared to come to closer quarters. What is the actual shape of a molecule? We know something of its relations with its neighbours, and something about its own internal arrangements. But we have as yet no decided ideas concerning its shape and architecture. With the ethereal electronic atom in the background of our minds, it is difficult to imagine anything so solid and definite as a molecule possessing a crystalline shape. But that is just what the new crystallography is arriving at. W. Barlow and W. J. Pope have recently put forward a remarkable theory which regards the whole of the volume occupied by a crystalline structure as partitioned out into polyhedra, which lie packed together in such a manner as to fill the whole of that volume without interstices, much like the cells in a honeycomb. Each polyhedron is the habitat of a single atom, and its volume is proportional to the lowest or fundamental valency of that atom. Here is another blow to the old idea that the atom merges all its properties in the molecule—a conception which is already shaken by Tutton's work, and by the facts of stereo-chemistry. Barlow and Pope's atomic spheres are deformable but incompressible, like Bucherer's electrons. They can be pressed into crystalline shapes, but they lose no bulk thereby.

It now becomes a matter of the close packing of spheres. For the mutual attraction of atoms makes them tend to approach each other as closely as possible. Now, there are two methods of closest packing, as everyone can verify for himself with bearing-balls or shot. One is cubic, and the other hexagonal. In the cubic method, horizontal and vertical translation are equivalent. In the hexagonal scheme, the ratio of horizontal to vertical translation is either 1 : 1·633, or 1 : 1·414. Taking all the elements which are known in crystalline forms, consisting, presumably, of identical spheres, it is found that 50 per cent are cubic and 35 per cent hexagonal, and in the latter the axial ratios agree closely with one or other of the above ratios.

This generalisation may even be extended to the binary compounds, such as NaCl, AgI, or ZnO, in which all atoms are of equal valency, and, therefore, probably of the same size. Of these, 68·5 per cent are cubic, and 19·5 per cent hexagonal, with a strikingly close approximation to the ratio 1 : 1·633.

LIQUID CRYSTALS

Le Bas has shown that the molecular volume of a series of normal paraffins in the liquid state at the melting-point can only be interpreted on the assumption that the atomic volume of carbon is four times that of hydrogen. This extends the principle of valency volumes to the liquid state. It is in this connection that Lehmann, and, subsequently, Vorländer and Jaeger, made their sensational announcement of the existence of liquid crystals, which show double refraction, dimorphism, and sudden changes of optical orientation. The doubts which were at first thrown on this discovery were simply the evidence of a prejudice in favour of a certain type of crystalline structure, the solid type. It surely cannot be maintained that the arrangement of molecules is necessarily altered by loosening the bonds holding them together. It is sometimes quite possible to read a printed sheet of paper after it has been charred and rendered extremely brittle and unstable: the essential structure remains. Moreover, we have, since Van der Waals, had too many proofs of the gradual transition from one state to the other to pronounce rashly against the persistence of crystalline arrangement in the liquid state.

Our attitude is different when some of these crystals imitate the phenomena of life sufficiently closely to be styled "living crystals." Lehmann has observed crystals which not only grow, but move about, and apparently move about in search of food, or, at least, go where they can grow most rapidly. All these properties are not confined to living matter. Bose's observations of fatigue and a rudimentary "memory" in metals are much more convincing and significant.

PIEZO-ELECTRICITY

An entirely different line of advance is that in which the compression of certain crystals, such as tourmaline or quartz, gives rise to electric charges of opposite kinds at the two ends. The compression, or its thermal equivalent ("pyro-electricity"), which squeezes electrons out of some of the atoms, is surely a most suggestive factor in crystalline theory. Do we not here approach a link between the electrical and the chemical atom? While we dig for radium, we have in these substances a means of investigating those very forces of which the radium rays are very striking, but not precisely illuminating, evidence.

The time is now ripe for throwing a bridge across the gap between the electronic atom and the chemical "brick." This bridge will, no doubt, be completed before many more years have passed.

CHAPTER XIII

CARBON COMPOUNDS

THE old distinction between mineral or inorganic chemistry and organic or vital chemistry no longer holds good. It is now agreed that vital phenomena do not transcend the rules of inorganic chemistry. They simply utilise them on a molecular scale, just as we do on a molar scale. The whole field of chemistry is one. Organic chemistry, so called, is simply the chemistry of one particular element, viz. carbon. But that element has the peculiar property of combining with itself in a variety of different ways, and so great is the variety of its combinations with itself and with other elements that no less than 65,000 different compounds of carbon have been discovered and described up to the present day. This vast array of substances is the subject-matter of the science which used to be called organic chemistry, but is now more appropriately termed carbo-chemistry, or the chemistry of the carbon compounds.

CARBON LINKAGES

The combination of two carbon atoms with each other may be illustrated by a simple experiment. Cut two tetrahedra, consisting of four equilateral triangles, out of cardboard, and in two of the edges of each which do not intersect, mount magnetised steel needles, so that there is a magnetic pole at every corner of the tetrahedra. Then three different combinations are possible. A north pole of one tetrahedron may adhere to a south pole of the other, leaving the other three corners of each tetrahedron free. Or two needles may coincide, leaving the other two needles free. Or, lastly, three corners may coincide, leaving only two corners free.

The carbon atom has, in all probability, such a tetrahedral shape. Its corners have, probably, some magnetic or (rather) electric polarity, though we do not yet know its precise nature. But we know carbon compounds which illustrate all the three types of linkage. Acetylene, C_2H_2, is an example of triple linking. If each link is represented by a dot, we may write it $H . C \vdots C . H$. In ethylene, C_2H_4, we have a case of double linking, which may be represented by $H_2 : C : C : H_2$; while in ethane, C_2H_6, there is only one link between the carbon atoms, $H_3 \vdots C . C \vdots H_3$.

It is usual to call the two former types "unsaturated" carbon compounds, and the last "saturated," because in this all the spare carbon bonds are used up to bind other atoms.

CHAINS AND RINGS

Whichever method of linking carbon atoms is adopted, it is evident that the linkages can be repeated indefinitely. If none but carbon atoms are employed, we may have chains of carbon atoms with free ends. But these free ends will have a polarity which, sooner or later, attracts other atoms of a suitable valency, and these will neutralise the free poles. They cannot be carbon atoms, as the latter are quadrivalent, and the free ends are never more than trivalent. Pure carbon, therefore, cannot exist in open chains. It must form a closed ring. Three different types of such rings are possible, and it is significant that carbon is known in three allotropic forms, viz. amorphous carbon, graphite, and diamond, though which type of linkage is represented by each is as yet an unsolved problem.

HYDROCARBONS

When a number of carbon atoms are joined in a single linkage, two corners of each atom are left free, and any univalent atom or molecule may attach itself to the free ends. When these atoms are all hydrogen atoms we get the large variety of the "hydrocarbons." The chain may be broken at any point, and an extra carbon atom, with its two hydrogen adherents, may be slipped in. Hence a whole series of compounds may be formed, whose molecules differ from the last by CH_2. When the hydrocarbons are saturated they are variously called paraffins, alkanes, or methane hydrocarbons, with a general formula

$$C_nH_{2n+2}.$$

Thus we get CH_4 (methane), $H_3C.CH_3$ (ethane), $H_3C.CH_2.CH_3$ (propane), $H_3C.CH_2.CH_2.CH_3$ (butane), and so on, up to hydrocarbons of the wonderful complexity of dimyricyl ($C_{60}H_{122}$).

Of unsaturated hydrocarbons, the following types are known:—

C_nH_{2n}.	Olefines, alkylenes, or alkenes.
C_nH_{2n-2}.	Acetylene series, with treble linkage.
C_nH_{2n-2}.	Diolefines, with double linkage.
C_nH_{2n-4}.	Olefinacetylene series.
C_nH_{2n-6}.	Diacetylene series.

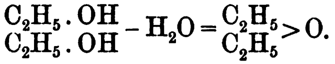
This enumeration shows that the number of combinations of carbon with hydrogen alone is very considerable. The reduction of hydrogen atoms in the unsaturated compounds is caused by a double or treble linking occurring at or near the ends of a chain.

OTHER CARBON CHAINS

Halides are formed by substituting chlorine for hydrogen atoms. Thus we have $CHCl_3$ (chloroform), CCl_4 (carbon tetrachloride), and $Cl_3C.CCl_3$ (perchlorethane).

Alcohols are formed by substituting hydroxyl, HO, for H. Thus methane (CH_4) becomes $CH_3 . HO$ methyl (alcohol). Ethane (C_2H_6) becomes ordinary or ethyl alcohol ($C_2H_5 . HO$). When more than one hydroxyl ion enters into combination, we get the higher alcohols, such as $HO . CH_2 . CH_2 . OH$ (ethylene glycol), which is called a dihydric alcohol. The "roots"—methyl, ethyl, propyl, etc.—are usually called alkyls, and their combinations with metals are becoming increasingly important in organic synthesis.

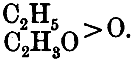
Ethers are obtained by subtracting water from alcohols, just as metallic oxides are obtained from hydrates. Thus



$$\begin{matrix} C_2H_5 . OH \\ C_2H_5 . OH \end{matrix} - H_2O = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O.$$

Ethyl alcohol – water = ethyl ether.

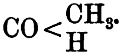
Esters, or compound ethers, contain one alkyl and one acid radical:—



$$\begin{matrix} C_2H_5 \\ C_2H_3O \end{matrix} > O.$$

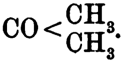
Ethyl acetic ester.

Aldehydes and Ketones both contain the carbonyl group CO; but whereas the former contain hydrogen atoms linked with the carbonyl, the ketones only have alkyls linked with them. Thus we have:—



$$CO < \begin{matrix} CH_3. \\ H \end{matrix}$$

Common aldehyde.



$$CO < \begin{matrix} CH_3. \\ CH_3 \end{matrix}$$

Dimethyl-ketone.

Fatty acids consist of carbon compounds attached to carboxyl (COOH), or to several carboxyl groups. The number of carboxyl groups indicates the basicity of the acid. Thus, acetic acid ($CH_3 . COOH$) is monobasic, while malonic acid ($COOH . CH_2 . COOH$) is dibasic.

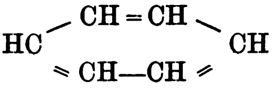
Carbohydrates are compounds of carbon, hydrogen, and oxygen containing six, or a multiple of six, carbon atoms.

The best known of these are cane sugar ($C_{12}H_{22}O_{11}$), starch $(C_6H_{10}O_5)_n$, and cellulose $(C_{12}H_{20}O_{10})_n$.

Besides the above, there are the albuminous and gelatinous substances, the hæmoglobins, enzymes, and other animal substances whose composition is not yet fully determined.

CYCLIC COMPOUNDS

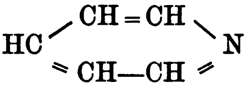
All the compounds so far enumerated consist of molecules forming open chains. From the fact of their containing the fatty acids, which include the distinguishing constituents of oils, fats, and butter, they are usually called the aliphatic compounds (from Greek *aleiphar*, fat); also methane derivatives, or acyclic carbon compounds. The other great division comprises those compounds whose molecules consist of closed chains. Their most general characteristic is that in their reactions with other substances the carbon atoms are, generally speaking, the last to break away from the molecule. They do not come away in groups like CH_2, but show a behaviour which suggests a more stable connection of the carbon atoms among themselves. These carbon atoms are at least six in number. The typical example is benzene, which may be written as follows:—



In this scheme (Kekulé's celebrated "benzene nucleus" figure, now usually placed upright) each carbon atom uses one of its bonds to bind a hydrogen atom, while the remaining three bonds go to the next carbon atoms on each side. Each of the hydrogen atoms can be replaced by a univalent atom or molecule, and thus we get the great array of benzene derivatives which, from their perfumes, have been styled the "aromatic series." They are also sometimes called the homocyclic or carbocyclic series, from the circumstance of their central rings consisting entirely of carbon atoms. Benzene, phenol (carbolic acid) C_6H_5OH, aniline $C_6H_5NH_2$, picric acid $C_6H_2(NO_2)OH$, benzaldehyde, or oil of bitter almonds, C_6H_5CHO, phenolphthalein (the valuable "indicator") $C_{20}H_{14}O$, are among the immediate derivatives of benzene. Naphthalene ($C_{10}H_8$) consists of two benzene nuclei joined, like Siamese twins, by two of their carbon atoms. Anthracene ($C_{14}H_{10}$) consists of three.

HETEROCYCLIC COMPOUNDS

When, in a carbocyclic molecule, one or more of the carbon atoms of the benzene nucleus are replaced by another atom or group of atoms, the resulting compound is called "heterocyclic." The first compound whose ring-constitution was definitely established was pyridine, which occurs in the oil obtained by the dry distillation of bones. Its structural formula is :—



Nicotine, morphine, strychnine, curarine, quinine, cocaine, and antipyrine are among the best known of the "alkaloids," all of which contain nitrogen, and belong to the heterocyclic division.

ORGANIC ANALYSIS

The above sketch gives no idea of the methods by which all this information has been gradually and laboriously acquired. But forty years of work cannot be disposed of in a few paragraphs. We have already indicated the manner in which empirical formulæ are arrived at. When the carbon, hydrogen, oxygen, nitrogen, and other constituents have been determined by combustion, and the usual reactions, the molecular weight has to be found. For this numerous methods are available, including those based upon vapour density, fusing-point, specific and latent heat, osmotic pressure, and optical properties. The result, arrived at almost entirely by physical methods, is the empirical formula, which confines itself to stating the number of atoms of each substance contained in a single molecule of it. When that is done, the real chemical work only commences. The new substance is put to a long series of chemical tortures intended to make it yield up all its inner secrets. The ease or difficulty with which its various atoms are removed, the manner in which they are detached (separately or in groups), the avidity with which they seize upon the atoms of other compounds—all this furnishes valuable indications of the structure of the molecule. The latter is like a new machine which is tested in every way, pulled to pieces and put together again, until every joint and every bond and link has been strained, tested, and broken, and until the innermost mechanism is laid bare to the inquisitive gaze of the chemical investigator. The number of tests and reagents is multiplying year by year. Quite lately, Molineri has discovered a valuable new reagent capable of discriminating the extent to which a carbon compound is unsaturated. It is ozone. He finds that unsaturated compounds, whether aliphatic or aromatic, containing double bonds, combine readily with ozone, whilst aliphatic compounds containing triple bonds, although uniting directly with a large proportion of iodine, do not absorb ozone. An interesting new method, lately applied to the separation of dyes, consists in allowing them to diffuse into jellies, into which different dyes penetrate with different velocities.

TERMINOLOGY

Some considerable diversity of opinion still prevails concerning the names of chemical compounds, old and new. It would, no doubt, be very desirable to have a uniform international system; but the historical and popular associations which cling to the older names cannot be easily disposed of, even were it desirable to do so. In 1892 a congress of chemists assembled in Geneva for the purpose of arriving at some understanding. They proposed to make all the alcohols end in "ol," aldehydes in "al," ketones in "on," and so on. But the system proved cumbersome and unworkable. Such names as "pentanolalon acid" could not be tolerated. A better plan is to promote a close understanding among the chief chemical publications in the various countries, and make them work towards a uniform system.

CHAPTER XIV

CHEMISTRY AND LIFE

THE animal body is a mechanism designed or evolved for the purpose of carrying out a certain series of mechanical operations serving certain non-mechanical ends. But it is more than that. It is a chemical laboratory, in which energy is transformed from one form into another, and substances are destroyed and rebuilt, to suit the requirements of the organism. It is both the machine which does the work and the engine which supplies the power. In exchange for the supply of power, the machine supplies the engine with the necessary fuel, and so the combination is kept going.

It is in the animal body, and more especially in the human body, that chemical problems reach their climax of practical interest. Innumerable processes are every day being carried out in the great organic laboratory which we all possess, and the majority of these processes are barely understood, even at the present day, not to speak of replacing them by artificial processes.

Nevertheless, a vast amount of work has been done, and it is proceeding at an increased rate. The next few years will probably witness some striking successes, towards which a converging series of researches are pointing.

FERMENTATION

When yeast was found to consist of living cells of a species of fungus, the conclusion that all fermentation is due to living organisms was a natural one. The great Liebig, indeed, could not agree with that conclusion, but said that fermentation was more probably due to some chemical substances secreted by the yeast fungus. This view has, after much discussion, been recently revived, and is steadily gaining ground. Since 1897, Buchner has been able to produce fermentation in sugar without adding a single yeast-cell to it. All that is necessary is to add to the sugar solution the juice pressed out from beer yeast and carefully freed from all yeast-cells. This juice, or, rather, that part of it which produces fermentation, has been called "zymase." It must be distinguished from another body, "invertine," which breaks up cane sugar into dextrose and lævulose, or right-handed and left-handed sugars, so called from their effect on planepolarised light. The common name of all such bodies is "enzymes," and their importance is growing so rapidly that there is a tendency to ascribe every obscure action to the presence of an unknown enzyme, just as, a hundred years ago, everything was attributed to the action of an unknown "vital force."

NUTRITION

The great goal towards which a vast army of workers are struggling is the synthetic production of food-stuffs. It must be acknowledged that the prospect is not a bright one, and to many people it is not even alluring; for the cheapening of food will inevitably lead to a great increase of the town populations, which are already sufficiently crowded. And there is an attractiveness about the fruits of the field which no chemical product, however attractively labelled, can rival. In any case, all the recent efforts to keep animals alive on "pure" foods, including the standard proteins, fats, and carbohydrates, have absolutely failed, and although this failure may be due to the lack of some unnoticed enzyme, or other constituent of ordinary food, it is quite possible that some irreducible organic origin may be essential to foodstuffs before they are capable of being utilised by the animal organism.

The proteins, those most complex and most elusive of organic substances, are being gradually unravelled. They are extraordinarily elaborate and varied, and none of them have, so far, been artificially prepared. But a number of fission-products have been identified. They are the comparatively simple bricks or elements from which animal protein is built up.

THE PROTEINS

A fairly successful agreement with regard to the nomenclature of the proteins has recently been arrived at between the Chemical Society, the American Physiological Society, and the American Society of Biological Chemists. Since the system agreed upon is likely to be of some importance in the future, the classification may as well be quoted here. Ten classes are recognised, and called, respectively: Protamines, Histones, Albumins, Globulins, Glutelins, Gliadins, Phospho-proteins, Sclero-proteins (albuminoids), Conjugated Proteins, and Protein Derivatives. The Conjugated Proteins are further subdivided into Nucleo-proteins, Chromo-proteins (hæmoglobins), and Gluco-proteins, while the derivatives include Meta-proteins (acid albumin, etc.), Proteoses, Peptones, and Polypeptides. It is these last which have been successfully built up by Fischer, who obtained a compound having the highest molecular weight ever yet attained artificially. It has an empirical formula, $C_{45}H_{72}O_{24}N_{18}$, and consists of two carbon chains linked together by carboxyl, CO. One of the chains is $CH(C_4H_9) . NH . [CO . CH_2 . NH]_3 . CO . CH(C_4H_9) . NH_2$, and the other is even longer: $[NH . CH_2 . CO]_3 . NH . CH(C_4H_9) . CO . [NH . CH_2 . CO]_8 . NH_2 . CH_2 . COOH$. Summing up the atomic weights, we get the appalling molecular weight 1213, which is about half that of some of the simpler proteins known. The name of this memorable substance, technically styled an "octadecapeptide," is almost as long as its structural formula, and is supposed to be quite as descriptive. It may here be appended as a curiosity:

l-leucyl triglycyl-*l*-leucyl triglycyl-*l*-leucyl octaglycyl-glycine.

It is well to remember that molecules of this magnitude are quite within the resolving power of the ultra-microscope, though I am not aware that it has been tried on it yet. The substance is a colourless, indistinctly crystalline powder, somewhat soluble in water. The solution becomes opalescent in the cold, and is precipitated by tannic acid.

SPIDER'S SILK

Although the polypeptide described would almost certainly be classed as a protein if found in Nature, it is in reality only a protein derivative. No true protein has yet been artificially built up. But Fischer sees a distinct prospect of building up one protein at least, which happens to be even more simple than the protamines. It is the silk fibre produced by the Madagascar spider. Like the fibre spun by the silkworm, it consists mainly of monobasic "amino" acids (i.e. acids containing the combination NH_2) the chief of which is Leucin (whose full name is isobutyl-amidoacetic acid $(CH_3)_2 . CH . CH_2 . CH(NH_2) . COOH$). It is curious that two very similar products should issue from two such different laboratories as the spinning-pap of a spider and the glands of a silkworm. The spider is a carnivorous animal, while the silkworm is an inexpensive vegetarian, and yet they both have managed the same organic synthesis which Fischer is now endeavouring to imitate. If the quest is successful, perhaps the ordinary food-proteins, such as white of egg and starch, may be made in the test-tube, and by and by that most useful of vegetable substances, cellulose, with its enormous complexity disguised in the formula $(C_6H_{10}O_5)_n$, may yield to the long siege whose first successes have given us Willesden paper, collodion, viscose, celluloid, gun-cotton, vulcanised fibre, and smokeless powder.

THE LIPOIDS

The lipoids are a new class of bodies, which received their name from Overton in 1901. The name is derived from Greek *lipos* (fat), and is applied to certain substances contained in the protoplasm of all cells, but more especially in their cell membrane. Overton drew attention to the fact that ether, chloroform, and other anæsthetics are soluble in the lipoids of the cell membrane, and that this solubility accounts for their capacity to enter the cells. The lipoids, on the other hand, are soluble in alcohol and ether, like the fats and fatty acids. Hence their name.

The lipoids are quite as important and vital as the proteins. In fact, they are even more vital, since they occur in special abundance in brain and nerve cells. They may be classified according as to whether they contain both nitrogen and phosphorus, or only nitrogen, or neither. The most important body of the last-named class is known as cholesterol, while members of the former classes are termed phosphatides and cerebrosides (brain substances) respectively.

CHOLESTEROL

When animal organs are treated with a mixture of alcohol and ether, and the residue is treated with cold acetone, cholesterol passes into solution. It is readily extracted from the white sheath of nerve-fibre by the acetone. As its name implies, it is an alcohol (according to modern usage, all non-alcoholic "ols" are spelt "ole"). It is, to be precise, an unsaturated monatomic alcohol of the terpene family. Its molecule probably consists of five benzene rings linked together. At all events, its empirical formula is $C_{27}H_{44}O$. Cholesterol is one of those interesting substances which make up Lehmann's liquid crystals. Such liquid crystals are met with in the cells of cancer, and in "fatty degeneration." This "fatty degeneration" is a mistaken term. The "fat" cells are really groups or strings of liquid crystals, consisting principally of cholesterol, and some fatty acid incorporated as "acid of crystallisation." But it must not be imagined that cholesterol is a deleterious substance. On the contrary, it is a substance intimately connected with life and growth. It occurs free in the brain, and also in the bile, and there is some evidence to show that the suprarenal gland is chiefly engaged in secreting it. The yolk of the hen-egg contains cholesterol, and this is all absorbed during the growth of the chick. Cholesterol has also a power of preventing certain actions of snake-poison. The venom of the cobra contains two toxins, one of which dissolves the blood corpuscles, while the other attacks nerve-cells. The former is neutralised by cholesterol, which also renders viper poison innocuous to the same extent. But viper poison also produces hæmorrhage, and this action must be stopped by means of hydrochloric acid.

Przibram has actually fed animals on cholesterol, and found that their resistance to certain poisons, such as bee poison, increased. Pascucci went so far as to prepare artificial blood corpuscles, and showed that they resisted agents tending to dissolve them if their membranes contained cholesterol.

OPSONIN

A class of substances still more mysterious than either the proteins or the lipoids are the opsonins, which are contained in the watery fluid of the blood. They have not yet been seen, but must be inferred from their action in "predigesting" microbes. The following are the main facts:

When microbes are introduced into the blood—say those called "staphylococcus" which produce boils—the white blood-corpuscles (leucocytes), like a well-drilled army, rush to the scene and do battle with the invading host. They usually dispose of them most effectively—viz., by eating and digesting them. But sometimes they do not. It is the business of the physiological chemist to find out when and why they do not. With this object, several experiments are performed. The leucocytes are extracted from a little blood (which contains 7000 in every cubic millimètre) and washed in several changes of water, until the blood serum is all separated from them. They are then mixed with microbes and brought to a blood-heat. But they seem to have lost all appetite for microbes. Nothing happens. If, however, a little blood serum is added, the battle soon rages furiously. Or if the microbes are first bathed in the serum, and then washed, they are also eaten up by the leucocytes. That substance in the blood, then, which "predigests" the microbes, and makes them appetising to the leucocytes, is called "opsonin," from a Greek word meaning "to prepare a banquet." It may quite possibly consist of invisibly small micro-organisms.

Opsonin is the latest discovery connected with the activity of that organic "police" which is so admirably organised for the defence of our bodies. The "opsonic index" of a patient is the proportional number of microbes of a given kind which his blood is capable of killing, as compared with the blood of a normal healthy person. It can be increased by injections of dead microbes of the same kind—a treatment lately practised by Wright with considerable success.

There are a number of different opsonins contained in human blood serum, and while a patient may have a low opsonic index (say 0·2) for tubercle bacilli, his opsonic index for other microbes may be quite normal. The injections are very minute; but the number of dead microbes injected is never less than a thousand million. Even so, they all fit on to the extreme point of a lancet.

BLOOD-PRESSURE

Not only the chemical composition of the blood, but its pressure, due to the action of the heart and the arteries, is powerfully affected by modern chemical agencies. One of the most remarkable agencies of this kind is adrenalin, obtained from small glands adjoining the kidneys, and first discovered in 1901 by Takamine, a Japanese chemist. It is a light yellow micro-crystalline substance with a slightly bitter taste. A one-thousandth per cent aqueous solution, injected into the veins in small quantities, increases the expansion and contraction of the heart to such an extent that the blood-pressure is increased two or three times. A two-millionth of a gram will produce quite a preceptible effect in an adult man, who thus becomes a detector capable of rivalling even the spectroscope in delicacy. In America, Crile succeeded in maintaining the heart's action in beheaded animals for ten and a half hours by means of continuous injections of adrenalin; and a dog which had been "electrocuted" was resuscitated by the same drug after fifteen minutes' apparent death. Adrenalin has a powerful constricting effect upon blood-vessels, and is used in surgery to prevent bleeding. It is prepared commercially on a large scale in Chicago from the suprarenal capsules of oxen, obtained from "Packing-town." It belongs to the homocyclic class of carbon compounds. It therefore possesses a benzene nucleus, but at two corners of the hexagon the H atoms are replaced by hydroxyl, HO, while to a third the chain $CHOH.CH_2.NHCH_3$ is attached.

Besides its useful effects, adrenalin also has some effects which are undesirable. It produces temporary diabetes, and this is not counteracted by its antagonist, choline, which neutralises its action on blood-pressure, the action of the heart, and the peristaltic motion of the intestine.

The field of biochemistry is a wide one; but no part of it can rival in importance that which investigates the working of the mysterious processes of the human organism.

THE PINEAL GLAND

The small outgrowth from the brain which Descartes described as the seat of the soul, on account of its being the only unpaired brain structure, is now regarded as a mere vestige, not of a single "pineal eye," but of a former third eye and the pineal gland, both of which are found in the lizard. Extracts from the human pineal gland produce apparently no physiological effects.

THE PITUITARY BODY

Not so with another riddle of the human body, which is now being solved. The "pituitary body," so called by the ancients because it was supposed to secrete the mucus of the nose, is an outgrowth from the base of the brain, weighing about half a gram. It is now known to be indispensable to life, producing certain "hormones" or chemical messengers which regulate the growth of the tissues. An overgrowth of the pituitary body produces "acromegaly" or gigantism. A giant must now be regarded, not as a person of enormous strength, but as an unfortunate being afflicted with the undue chemical activity of a small organ situated just over the roof of his mouth.

CHAPTER XV

THE CHEMISTRY OF METALS

METALLOGRAPHY owes much of its recent development to the commissions appointed in various industrial countries for dealing with the theory of metallurgical processes. It is now clearly recognised that many metals possess allotropic forms, which, in many points, recall the differences in states of aggregation. Lother Meyer says: "The change of one allotropic modification into another is so similar to the change of one state of aggregation into another, that, strictly speaking, the three states of aggregation of any substance whatever must be described as three allotropic modifications of it. . . . The melting of ice, for example, is the conversion of the light into the heavy modification of water."

The metals which have, so far, been found to exist in allotropic forms are: Antimony, arsenic, lead, iron, iridium, selenium, silver, tellurium, zinc, and tin. The similarity between allotropic change and change of state of aggregation is brought out by the following facts:—

1. In both cases there is an evolution or absorption of heat.
2. The change occurs normally at a definite temperature.
3. Undercooling is observed in both changes.
4. The presence of a third body may profoundly influence the transformation.

COOLING CURVES

The study of the allotropic modifications of the metals is greatly facilitated by the delicate methods now available for measuring and recording temperatures. Mercury thermometers are now used for temperatures as high as 600° C. But as ordinary glass softens at 500°, fused quartz must be employed for the thermometer tubes, and the space above the mercury must be filled with gas, so as to raise the boiling-point of mercury. For higher temperatures the thermo-couple still holds the field, although a number of new methods are now available, including that based upon the resistance of platinum and that based upon Stefan's law of radiation.

Once obtained, the cooling curves may be plotted in three different ways. The time-honoured method is to plot the temperatures as ordinates, and times as abscissæ. The curve then usually consists of sloping portions joined by short horizontal pieces. In another method, due to Osmond, the abscissæ are temperatures, and the ordinates are rates of cooling. This gives pointed peaks at the temperatures of transformation. Dejean's method (1905) gives, instead, the change of temperature per unit time, and gives it automatically by means of an arrangement of two galvanometers, and a totally reflecting prism, due to Saladin.

ALLOYS

The immense importance of the new thermo-chemical methods is best realised by considering the remarkable advances recently made in the study of alloys. Not very long ago alloys were considered the most puzzling and unaccountable mixtures of the elements. Roozeboom's application of the Phase Rule, first to mixed crystals, and next to alloys, has enabled us to predict most of the transformations and changes of properties which occur when the proportions of the ingredients are altered. It is true that the Phase Rule tells us nothing about quantities direct; but it enables us to tell when perfect equilibrium has been reached, and no further products may be expected. The Phase Rule has already been dealt with in Chapter IV. The equation representing it is—

$$F = C + 2 - P,$$

where F is the number of variabilities or degrees of freedom, C is the number of components, and P the number of phases. If (as in most metallurgical operations) differences of pressure are negligible, the rule reduces to—

$$F = C + 1 - P.$$

If a system consists of, say, tin and lead, and the only phase present is the liquid melt, we have $P = 1$, $C = 2$, and hence $F = 2$, which means that the two variables, temperature and concentration, can both be changed without changing the number of phases—i.e. without either of the metals crystallising out. But if lead crystals are admitted as a possible phase, $F = 1$, and a given temperature determines the concentration, and vice versa. If the temperature, for instance, is 250° C., there must be 65 per cent lead and 35 per cent tin in the melt, in the presence of lead crystals. Any other system at that particular temperature is either solid or perfectly liquid.*

If solid tin is also to be present, $P = 3$, and $F = 0$. The temperature and concentration are absolutely fixed, and we have the "eutectic" alloy 32 per cent lead and 68 per cent tin, with a temperature of 180° C.

Binary and ternary alloys are the only ones hitherto brought into line, and their investigation has been greatly facilitated by the use of rectangular diagrams for the latter.

The best way of charting these properties of alloys is to draw curves with percentage compositions as abscissæ, and either freezing-points or specific volumes as ordinates. In the freezing-point curve, definite compounds are indicated by maxima in the temperature at which freezing begins. In the specific-volume curves each angular point corresponds to a definite compound, so long as no solid solutions are contained in the system.

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* See Goeren's *Introduction to Metallography*. Longmans. 1908.

BEARING METALS

The structure of ternary alloys is of great practical importance in such compounds as bearing metals, which are now sold in great variety under all sorts of fancy names. The characteristics of a good bearing metal are that it should wear uniformly, and give the minimum of heat. If the metal is soft and homogeneous, like pure lead, single particles are liable to be torn off, and to eat into the journal. This leads to heating and to the squeezing-out of the metal. If the metal is too hard, the friction is likely to be confined to a few points. If, as in the bronzes, soft crystals are embedded in a hard eutectic matrix, the crystals are rapidly worn away, so that the shaft runs on the hard matrix alone, and hot running sets in.

The best metal is that in which hard grains are embedded in a soft matrix, since an excessive bearing-pressure simply presses the crystals into the matrix, and the form of the bush adapts itself exactly to that of the journal. This requisite is fulfilled by most white metals.

MICROSCOPIC STUDY OF METALS

A great deal of useful information concerning such crystalline structures has been gained by means of micro-metallography, or the microscopic study of polished and etched metallic surfaces. The polishing is a process requiring considerable skill, as the difficulty of obtaining a good mirror surface giving a uniform field is great, and a slight error is apt to lead to the surface being torn off.

A piece of the metal to be examined, measuring 1 × 1 × ½ cm. is cut out and ground with a file or with emery. The grinding on any particular grade of emery is continued until the scratches produced by the preceding grinding are completely effaced. For this purpose, the section is rotated each time, so that the induced scratches are at right angles to the existing ones, until the latter are no longer discernible. The finest emery disc is replaced by a wooden one covered with cloth on which levigated jeweller's rouge is spread by means of a colouring brush. This is continued until no scratches are seen under the microscope. The whole process takes about two hours.

The method just described is that used at the Berlin Metallographic Institute, whose Director, Professor Martens, has furnished a name for a well-known iron-carbon alloy. Le Chatelier has devised another and rather more expeditious method, in which alumina alone is employed.

The polishing is followed up by various devices for bringing out the different constituents of the metal. One of these is relief-polishing, in which the softer and more easily wearable constituents are removed by the finest levigated rouge, which is spread over a piece of stretched parchment, the latter being scrubbed with a brush until only the finest particles remain in the pores of the parchment.

Another device is heat-tinting, based upon the fact that many constituents oxidise on heating more rapidly than others. This is the only method capable of microscopically discriminating between carbides and phosphides. The sample is quenched in mercury as soon as the correct tint is reached.

ETCHING

Etching is done with nitric acid (iron and its alloys), picric acid (iron-carbon alloys), hydrochloric acid (quenched iron alloys), sodium picrate (for cementite), fused calcium chloride (iron and steel at high temperatures), concentrated potash (zinc-copper alloys), or ammonia (copper). Tincture of iodine or cuprammonium chloride are also used in some cases; and Le Chatelier has combined salammoniac etching with electro-chemical decomposition by making the sample the anode in an electrolytic cell.

Microscopes have been specially designed for observing the surfaces by reflected light. A side illumination is secured by a mirror, and a vertical illumination either by means of a total-reflection prism contained within the microscope, or a piece of plane glass mounted between the objective and the specimen, at 45° to the axis of the microscope, so that a beam coming from the side is thrown perpendicularly on to the specimen, and reflected by it along the axis of the microscope.

Of late, microphotography has been successfully applied to the microscopic study of metallic surfaces.

ELECTRO-METALLURGY

Chemical industry has a tendency to localise itself more than other industries owing to the unequal distribution of its raw material. It is, therefore, quite a common thing to see an industry becoming the monopoly of a particular country, like the coal-tar products and potash of Germany. A somewhat similar feature, due to a very different cause, is the localisation of electrolytic processes in countries which, like France, Switzerland, Norway, and the United States, are liberally supplied with water-power.

ALUMINIUM

Practically all the world's supply of aluminium is now manufactured either by the American Hall process or the French Heroult process. The Cowles process, started in 1886, was superseded in 1892, four years after Hall started his works at New Kensington in America. The

Hall process starts with cryolite, fluorspar, and alumina. When these are melted together, the alumina dissolves in the fluorides of the cryolite, and on electrolysing the mixture between carbon electrodes, fused aluminium separates at the cathode. The Heroult process, which started originally with pure alumina, has been gradually modified until, at the present moment, it can be hardly distinguished from the Hall process. Seven out of the nine European aluminium works use the Heroult process. One of these is the factory which utilises the famous Foyers waterfall near Loch Ness, in Scotland. Since the Heroult patents lapsed in 1902, the manufacture of electrolytic aluminium is now free from royalties, and the metal will probably be greatly cheapened. So far, the chief utilisation of aluminium has taken place in metallurgical operations, but aluminium utensils, which tarnish less than silver, are coming more into favour.

THERMIT

One of the most interesting applications of aluminium is that in which powdered aluminium is mixed with ferric oxide and ignited. An intense combustion is the result, in the course of which the aluminium deprives the iron of its oxygen, and the latter escapes at a white heat. Such a mixture is now manufactured under the name of Thermit, and used for welding defective castings, broken mainshafts, stern-posts of steamers, electric tram-rails, and other iron objects which cannot very well be transported to an iron-foundry. The weld produced is as strong as the original casting.

If it were possible to use bauxite instead of cryolite, the process of obtaining aluminium would be much cheapened; but as the utility of aluminium depends greatly upon its purity, it is probable that a cheap purifying process will be more effective in bringing aluminium into general use.

That event will mark a new era, as aluminium is one of the commonest of all elements.

ELECTRIC IRONWORKS

The electro-metallurgy of iron and steel had a curious origin. The collapse of the calcium carbide boom in 1900 had rendered idle a large number of water-power stations in the south-eastern districts of France. Some new metallurgical application of electric power was therefore urgently required to provide a load for this generating and furnace plant, and to earn interest upon the capital expended upon its erection. The production of ferro alloys was the first step towards the utilisation of this idle plant for other purposes.*

The report of the Canadian Commission, issued in 1904, was favourable to the new electrolytic methods of iron and steel manufacture, and gave a great fillip to their introduction. For steel-refining, the Heroult, Keller, Gin, Stassano, Kjellin, and Colby (induction) processes are now worked in France, Germany, Italy, Sweden, and America; and iron-smelting has also been attempted experimentally with considerable success. The amount of steel already dealt with by these processes reckons by thousands of tons.

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* See Kershaw's *Electrometallurgy*. Constable, London. 1908.

CHAPTER XVI

INDUSTRIAL CHEMISTRY

In his Presidential Address to the Chemical Section of the British Association, meeting in Dublin in 1908, Professor F. S. Kipping drew a lugubrious picture of the state and outlook of British Chemical Industry. He said: "The fiftieth anniversary of the epoch-making discovery of mauve was held only two years ago, and the proceedings are still fresh in our recollection; the pæans of congratulation addressed to the discoverer * (now, alas! no longer with us) were marred by a plaintive note—a note of lamentation—over our lost industry, the manufacture of dyes. The jubilee of the founder of the colour industry in this country was also the occasion for pronouncing its funeral oration. If this were the full extent of our loss, we might bear it with equanimity; but it is not so much what has already gone as what is going and what may go, that are matters of such deep concern. Those who doubt the seriousness of our condition may find statistical evidence, more than sufficient to convince them, in the technical journals and in the Board of Trade reports of recent years."

"The facts there disclosed," he continued, "show that in the manufacture of 'fine chemicals,' including perfumes, alkaloids, and crude coal-tar products, as well as dyes, the decadence of our industry is far advanced; in the case of

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* Perkin, who was the first to produce an aniline dye (mauve) upon a technical scale in 1856, by acting upon aniline with bichromate of potash and sulphuric acid.

heavy chemicals our position, perhaps, is not quite so serious at the present moment; but the future is dark and threatening. Chemical industries are so intimately connected and dependent on one another, that the fate of one may determine the fate of all; the by-product of one process is often the raw material of another. Who, then, can deny that the patience, perseverance, and high scientific skill which have built up the colour industry abroad, if applied, as they have been and are being applied, to the manufacture of heavy chemicals, will not soon defy all competition from less progressive countries?"

During the Perkin jubilee celebrations, Professor Carl Duisberg emphatically denied that there was any prospect of saving the British coal-tar industry. He attributed the success of his countrymen to a rare combination of theory with practice, which, he said, was the monopoly of Germany. The story of the German discoverer of a new chemical substance, whose chief satisfaction was derived from the circumstance that it could never be of any possible use to anybody, indicates and somewhat exaggerates the German idealistic tendency, which has, in the long run, brought forth such abundant fruits.

The Patent Act of 1908 is leading to the establishment of branches of foreign chemical manufactories in the British Isles, and although these are largely staffed by foreigners, this influx of the pick of foreign brains must in the end prove as beneficial as it was in the days of the Huguenots.

Professor R. K. Duncan, of the University of Kansas, has inaugurated a system of Industrial Fellowships, tenable at universities, and endowed by firms engaged in chemical industries who wish trained chemists to undertake researches with a view towards solving given problems affecting their industry. These Fellowships are tenable for two years, and are of the value of £125 to £250 per annum. All discoveries made by Fellows are the property of the firm which founds the Fellowship; but the Fellow is regarded as the inventor, and takes one-tenth of the proceeds of his discovery. At the expiration of his tenure, the Fellow is bound to furnish a comprehensive monograph on the problem proposed, which may be published by the University after the expiration of three years. In addition, the Fellow is now bound to give two hours a week gratuitous instruction in the University. The scheme is already doing good work, and seems likely to solve the long-standing problem of bringing the great resources of science to bear upon pressing industrial problems.

COAL-TAR

Nowhere has the benzene nucleus played a more important part than in tracing the connection between the various "aromatic" compounds derived from coal-tar. The first to isolate benzene from the light oil obtained by the destructive distillation of coal was Mansfield, who in 1847 died from burns inflicted by the substance he had himself discovered. Aniline, or amidobenzene $C_6H_5(NH_2)$, is obtained by replacing one of the hydrogen atoms of the benzene ring by the monad group NH_2. This is done by first converting benzene into nitrobenzene, $C_6H_5(NO_2)$, by treating it with nitric acid. When nitrobenzene is reduced by a mixture of iron filings and hydrochloric acid the chlorides of iron and of aniline are formed. The aniline is liberated by addition of an alkali, and separated by distillation. The smallest trace of aniline may be detected by adding the substance to an aqueous solution of an alkaline hypochlorite, when a splendid violet coloration is produced. Aniline mauve was discovered in 1856, magenta (fuchsine) in 1858, and from the latter aniline blue, violet, and green were derived in quick succession. Aniline black, discovered by Lightfoot in 1863, is still defying a full analysis. But the constitution of the other aniline dyes is now so well known that many of them are prepared synthetically, from oxalic acid, formic aldehyde, and carbonyl chloride.

One of the most momentous results of these researches was the synthesis of alizarine from a constituent of the heavier coal-tar oils, called anthracene. The discoverers of this synthesis, Graebe and Liebermann, were led to it by finding that the alizarine obtained from the madder root is reduced to anthracene by zinc dust. This was followed by the azo-dyes, mostly salts of amido-azo-benzene, of which now some two hundred are in the market.

The destruction of the Alsatian, French, and Algerian madder plantations by the synthesis of alizarine has had an even more disastrous sequel in the artificial production of indigo by Heumann on behalf of the Badische Anilin und Soda-fabrik in 1897, a discovery which means that millions of pounds will pass from British into German hands. The encouragement offered by the Government of Bengal to researches on indigo are hardly likely to save the vast indigo plantations of India from utter extinction.

Dyes are not the only commercial products obtained from coal-tar, once regarded simply as a very troublesome waste product. Another coal-tar hydrocarbon, toluene, or methyl-benzene, $C_6H_5(CH_3)$, gives rise to saccharine. Others are transformed into explosives by introducing nitrogen into their molecules; others, again, are made into carbolic acid, picric acid, salicylic acid, and other well-known compounds. New perfumes are being brought out in large numbers. Cyanides, ferrocyanides, and sulphocyanides are made from the residues of the gasworks, and some of the most popular new photographic developers, such as the amido-oxy-compounds rodinal, edinol, methol, and amidol, owe their origin to the same uninviting but inexhaustible source.

GLASS

"In spite of the development of mechanical appliances, in spite of the unquestionable expertness of their management, the glassmen conduct their business on the basis of the motto, 'Save at the spigot and waste at the bung'—the story of American glass manufacture is a story of confusion and waste." This is the severe indictment of American glass-blowers' methods by Professor Duncan,* who contrasts the chemical ineptitude of Americans with the thoroughly scientific attitude of the authorities at Jena and Charlottenburg. He mentions a case in which a large manufacturer of coloured glass for church-windows wished to make ruby glass with copper instead of gold. He, therefore, purchased a "secret" formula for the manufacture of copper ruby glass. But on applying it he found that the glass came out uniformly with a delicate green colour. On consulting a chemist, they found that the formula was a well-known French formula for ruby glass. It also came out that they were using red lead, Pb_3O_4, instead of litharge, PbO; stannic oxide, SnO_2, instead of stannous oxide, SnO; and black oxide of copper, CuO, instead of cuprous oxide, Cu_2O. All these materials used were oxidising instead of reducing agents, and the essential necessity of keeping the copper in the "cuprous" condition was entirely lost sight of. Many "practical" men also use white arsenic, although it makes no difference whatever to the result, and is all evaporated by the time the glass is cast.

It must be admitted that glass is still a puzzle, even to the chemical theorist. There are notable divergences of opinion as to whether glass is a mixture or a compound. That it is in an essentially unstable condition is well known. The rarity of ancient specimens of glass proves that glass devitrifies in a few centuries. Glass is a substance which is, so to speak, arrested in its natural process of crystallisation. The vitreous structure of volcanic products which reach the surface contrasts suggestively with the crystalline structure of the same rocks when slowly cooled at a great depth.

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* See his *Chemistry of Commerce*, Harper. 1907.

The dispute concerning that curious substance, ultramarine, discovered by Gmelin in 1828, is an example of the difficulties which attend the settlement of questions concerning the vitreous state. Some authorities describe it as a compound, a sulphosilicate; others, again, regard it as a mixture. The latest theory, due to Knapp, is that it is a "solid solution" of the colouring substance in the vitreous ground-mass.

The great Jena glass industry was founded by two men, Abbe and Schott, who recognised the importance of investigating the properties of glass systematically by means of all modern physical instruments and resources. When they began their work, the information available was confined to five glass-forming oxides; these were silica, potash, soda, lead oxide, and lime. To these they added boron, phosphorus, lithium, magnesium, zinc, cadmium, barium, strontium, aluminium, beryllium, iron, manganese, cerium, didymium, erbium, silver, mercury, thallium, bismuth, antimony, arsenic, molybdenum, niobium, tungsten, tin, titanium, uranium, and fluorine, determining in each case what optical and other properties were affected by the addition of each substance, and to what extent they were so affected. They found, for example, that boric acid lengthens the red end of the spectrum relatively to the blue, and that fluorine, potassium, and sodium have the opposite effect; and they could govern the absorption of the visible, infra-red, and ultra-violet rays almost *ad libitum*. The firm of Zeiss, in Jena, has produced some 2000 new optical glasses, which may be classified as follows:—(1) Barium and zinc silicate crown; (2) borosilicate crown; (3) heavy baryta crown; (4) baryta flint; (5) antimony flint ("telescope flint"); (6) borosilicate flint; (7) borate glasses; (8) phosphate glasses. The telescope flint has a refractive index of 1·5286, and a dispersion 0·0125 between the lines C and F. A special glass is also now made under the name of "uviol," for the transmission of ultra-violet light; but it looks as if the best substance for ultra-violet optics were rock-salt, which, according to Pflüger, possesses great transparency for ultra-violet rays combined with a high dispersion. If a prism with an angle of 60° is cut out of the three substances fluorspar, quartz, and rock-salt, they show, for rays of wave-lengths $185\mu\mu$. to $231\mu\mu$., dispersions of 3°, 6°, and 27°, respectively. The deterioration of the surface of the rock-salt prism may be guarded against by cementing a thin plane-parallel plate of quartz to its surfaces by means of glycerine; but the quartz will absorb all rays shorter than $230\mu\mu$. It is also possible to construct achromatic lenses of rock-salt and quartz, a triple combination being used, with the rock-salt in the centre. This makes a most efficient spectrograph.

As regards coloured glasses, it is now certain that ruby glass owes its colour to a colloidal suspension of gold in it. This was proved definitely by Siedentopf and Szigmondy by means of their ultra-microscope, in which particles beyond the resolving power of the ordinary microscope are rendered visible, like motes in a sunbeam, by a strong source of light impinging upon them at a particular angle. On counting the number of particles visible in a given volume, the weight of these particles may be calculated from the known amount of gold present. The result shows that the gold particles closely approach the dimensions of the largest molecules. To render the calculation trustworthy, it is, of course, necessary to make sure that the particles are of fairly uniform size, so that none may remain invisible: it is also desirable to ensure that none but the particles actually in the field of view are illuminated.

The Jena investigations have not been confined to optical glasses. Artificial gems have grown into a large industry since rubies have been manufactured on a technical scale. But the most remarkable advances have been made in the control of the mechanical and thermal properties of glass. The cracking of glass by heat is always due to its unequal expansion. But it is now possible to obtain glass vessels which do not expand at all under heat. This is accomplished by combining an outer layer of high expansibility with an inner layer of low expansibility in such a manner that the volume remains independent of the temperature. Two glasses of different expansibilities have even been welded together so as to form a combination capable of resisting sudden applications of heat and cold. A water-gauge tube for steam-boilers made in this manner may be heated in oil to 230° C., and immediately plunged into cold water without flying.

THE ELECTRIC FURNACE

Henri Moissan, in bringing the heat of the electric arc to bear upon chemical reactions, founded a new chemical industry, and inaugurated a new era of chemical research. His electric furnace is simplicity itself, consisting as it does of two arc carbons enclosed between blocks of limestone. The temperature obtained is 3500° C., that being the boiling-point of carbon. It enables us to make a number of substances combine with carbon, thus forming the carbides whose importance is looming so large of late—calcium carbide for acetylene, magnesium carbide for hydrogen, aluminium carbide for marsh gas, and for winning aluminium from china clay. Conversely, a number of metals are obtained from their oxides—barium, strontium, and calcium itself. The power of Niagara Falls drives Acheson's carborundum and graphite works, distils red phosphorus from mineral phosphates, and produces most of the world's supply of calcium carbide in the Union Carbide Company's manufactory. In Paris, thirty or forty rare metals and alloys are produced on a commercial scale. Chromium, tungsten, molybdenum, and silicon are now on the metal market, and a whole factory is devoted to ferrosilicon alone. The electric furnace has annexed a whole range of temperatures to our resources which a few years ago were even beyond measurement, not to speak of commercial utilisation. Nor does 3500° C. reach the limit of available temperatures. Sir Andrew Noble has attained the astonishing figure of 5200° C. by exploding cordite in closed vessels, and we may hear at any moment of new and unlooked-for triumphs of chemistry which may revolutionise many of our existing industries, and create new ones hitherto undreamt of.

CHAPTER XVII

THE ATOMIC THEORY

"THERE is one branch of actual observational knowledge in which this identity of the molecules of a substance asserts itself with special strength: if the molecular theory had not been introduced on the evidence of the laws of definite and multiple proportions in chemical compounds, it must have demanded recognition as a result of a study of the crystalline structures of bodies. We call to mind that correspondences are now coming to light by which it is becoming possible to reason regarding the type of the molecule, and the geometrical grouping of its constituent atoms, from measurement of the crystalline aggregate. In such cases the single molecule would itself be the ultimate formative crystalline element. Where an atom has a higher valency, it must, according to any formula of special chemical constitution, aggregate more atoms round it and in touch with it in the molecule. It must, on that account alone, itself occupy, or exist in, a larger central space. In this way, greater atomic volume would be, in general, a result of greater valency, while the atomic volume will always be nearly the same in similar surroundings. The very striking recent investigations to ascertain how far the structure of the crystal is determined by the arrangement of the atoms in its molecule, on the basis that equi-valent atoms require about the same atomic volume, are known to all of us here." In these words did the secretary of the Royal Society* specify the three fundamental laws embodied in Dalton's atomic theory.

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* Sir J. Larmor, Wilde Lecture, 1908. Mem. Manchester Lit. and Phil. Soc., May 20, 1908.

Constant proportion, multiple proportion, and the regularity of crystalline structure are the stubborn facts which have forced chemists again and again back upon the conception of identical and irreducible atoms. Voigt has contrasted the domain of crystals, where all is definite, orderly arrangement, with that of liquids and gases, where physical properties are merely average values which belong in the statistical sense to crowds of jostling molecules. Helmholtz, on the other hand, used to remark that organic chemistry progresses steadily and surely, but in a manner which, from the physical standpoint, appears not to be describable as quite rational. Yet Larmor now acknowledges that the space formulæ of chemistry have more than a merely analogical significance, and that the many instances (specific heat, refractive index, etc.) in which the physical properties of the compound molecule can be calculated by summing up those of the constituent atoms are difficult to explain unless we suppose that chemical combination is not so much a fusion or intermingling of the combining atomic structures, as rather an arrangement of them alongside each other under steady cohesive affinity, the properties of each being somewhat modified, though not essentially, by the attachment of the others.

Recent researches, both in physics and chemistry, have somewhat shaken our belief in the unchangeable Daltonian atom. The electrical view of the atom makes it a delicately balanced structure of great complexity, while the phenomena of radioactivity suggest that the delicate balance is occasionally upset, whereupon the atom disintegrates with explosive violence.

ATOMIC ENERGY

Whatever may be the outcome of the new atomic theory towards which we are groping our way, it is very probable that much light will be shed on the nature and origin of matter, or, rather, of mass. The most suggestive hypothesis recently put forward is that propounded by Einstein in 1905, according to which mass and internal energy are identical. He showed that if the velocity of light is a constant quantity everywhere, then energy itself must have momentum and energy of motion, and hence, also, an inertia of its own. This inertia is an equivalent of mass, though not of weight. In other words, a quantity of energy may resist acceleration and retardation, but may not, for all that, attract another quantity of energy.

This astounding proposition has received further support since then. Planck, on the strength of certain data supplied by radiation and by thermodynamics, maintains that all energy is emitted, or transferred, in certain irreducible elementary quantities; that, in fact, energy itself has something resembling an atomic structure. Gilbert Lewis goes so far as to suggest that energy has weight as well as mass, and that the sun's rays, therefore, contribute to the sun's attractive power, though in the case of very small bodies the pressure of radiation masks this force.

To come down to figures, both Einstein and Lewis conclude that the energy contained in a gram of matter (we might say, the energy constituting that gram of matter) is no less than 900 trillion ergs (or 9×10^{20} ergs), that figure being the square of the velocity of light in centimetres per second. If this figure is correct, it means that an ounce of matter—any sort of matter—contains enough energy to blow nearly a million tons right off the earth.

How such prodigious energy is stored within the atom is still a mystery. But the phenomena of radioactivity have familiarised us with an astonishing reserve of energy contained within the atom, and absolutely unsuspected a few years ago. They have also brought home to us the suggestive fact that the mass of an atom may, in some rare cases, undergo a gradual diminution, accompanied by a relatively enormous evolution of energy. All this lends an air of reality to Einstein's bold speculation, and imparts a new interest to the atomic weights of the elements.

THE PERIODIC LAW

Attempts to arrange the elements in groups according to their atomic weights were many before the coming of Mendeleeff. Prout's hypothesis suggested that the properties of the elements should be somehow connected with the properties of whole numbers. The properties of numbers are nearly as varied as those of chemical elements, and the temptation to find a common cause underlying both complexities proved irresistible. Doebereiner (1829) arranged the elements in triads which either increased in arithmetical progression or were nearly equal. Pettenkofer (1850) pointed out that the number 8 recurred in many differences of atomic weights, either itself, or a multiple of it. J. H. Gladstone (1853) endorsed the remark of Berzelius that "Bodies which present the same properties, up to a certain point, have certain relations between their atomic weights," and gave numerous examples. Cooke (1858) arranged the elements in six classes, each derived from a fundamental element by a homologous series, like the carbon compounds of organic chemistry. Odling followed in 1857 with a classification into thirteen groups, and in the following year Dumas proposed another grouping based upon the chemical "equivalents" instead of the atomic weights.

None of these systems, however, succeeded in getting at the fundamental truth embodied in the term "periodicity." They all implied and asserted that the properties of substances are functions of their atomic weights; but it was only in the early sixties that the term "periodic functions" appeared. The first suggestion of periodicity was contained in De Crancourtois's Telluric Helix (April, 1862). A cylinder had its base divided into sixteen equal parts, and a scale of atomic weights was attached to its generatrix. On the cylinder was traced a helix, inclined at an angle of 45° to the axis. The elements were thus divided into groups, each differing from the previous group by sixteen.

Newlands, who published his scheme in the *Chemical News* in February, 1863, is sometimes described as the real discoverer of the periodic law. But his eight groups are not strictly arranged according to atomic weights, transpositions being made in order to bring elements of the same family together. He regarded the number 7, or some multiple of 7, as the fundamental difference between analogous atomic weights, and described his system by what he called the Law of Octaves. When he read his paper before the Chemical Society, Professor Foster facetiously asked him whether he had tried the result of arranging the elements in alphabetical order!

The real credit of discovering the periodic law must undoubtedly be accorded to Professor Mendeleeff, of St. Petersburg, who published his first paper, entitled "An Attempted Classification of the Elements, Based on their Atomic Weights and Chemical Analogies," early in 1869. It was followed early in 1870 by Lothar Meyer's paper on "The Nature of the Chemical Elements as a Function of their Atomic Weights," published in Liebig's *Annalen,* in which Meyer acknowledges Mendeleeff's priority.

However great the success with which Mendeleeff grouped the elements according to their physical and chemical properties, his system would have attracted little attention but for his striking success in predicting the properties of undiscovered elements. One of the gaps he filled up by an element, which he called "eka-aluminium," and which, he said, would be found to possess the following properties:—Atomic weight, 69; forms an oxide of the type R_2O_3, soluble in ammonia, and a chloride, RCl_3; is capable of forming alums; is easily obtained in the metallic state, with density 5·9; is not easily oxidised, but easily fusible; its chloride is volatile; it may be discovered by the spectroscope. All these properties were literally matched by those of Gallium, discovered by Lecoq de Boisbaudran in 1875. Scandium followed in 1879, and Germanium in 1886. These signal triumphs appealed to the popular imagination as no other chemical discoveries had done before. They appealed in the manner of the discovery of Neptune in the field of astronomy. For the first time chemists were in possession of a system of classification which had to be taken seriously. Not only could new elements be discovered, but Mendeleeff, being in possession of the new master key, felt strong enough to correct the accepted atomic weights of uranium, indium, yttrium, titanium, and osmium. The new atomic weight of uranium, 240, placed it at the bottom of the heaviest elements, the last heir of the long evolution of falling temperatures, and the progenitor of that modern wonder among the elements—radium.

Lothar Meyer's best work was done on Atomic Volumes, which he plotted in his well-known curve, in which the periodicity of melting- and boiling-points, and of electric character, is brought out in a striking manner.

Much work has since been done: by Carnelley on melting-points and organo-metallic compounds; Ditte, Trooste, Hautefeuille, Lockyer, Mitscherlich, Rydberg, Watts, and Kayser and Runge on periodicities in the spectra; by Carnelley and Capstick on colours of compounds; by Cuthbertson and Metcalfe on refractivities; by Rydberg on hardness; by Richards (1907) on compressibility and expansion; and by McClelland on the absorption of radium rays. In all these departments the periodic law has acted as a safe guide, so that the Periodic Law—that "the properties of the elements are periodic functions of their atomic weights"—may now be taken as completely established. Since

Mendeleeff's time, it has been formulated and tabulated in various different ways, notably by the spirals designed by Crookes and Johnstone Stoney respectively. The former is important in connection with modern transmutation projects, and the latter makes the new gases helium, argon, krypton, and xenon fall into their appointed places in a remarkably elegant manner.

NUMERICAL RELATIONS

Numberless attempts have been made to find a general formula for the atomic weights of the elements. Mills, Carnelley, Vincent, Minet, and Delauney are some of the most successful investigators along this line. The simplest formula, $W = (n + 2)^{1 \cdot 21}$, is due to Vincent. In this formula, W is the atomic weight, and n is a whole number from 3 to 60. But all the formulæ proposed attempt to approximate closely to the atomic weights actually observed, which are, as a rule, not whole numbers, but numbers followed by several decimals. A diametrically opposite course is taken by Alfred Egerton, who quite recently (1909) arranged the elements on the supposition that their atomic weights are multiples or submultiples of that of the oxygen atom, the divergences from whole numbers being produced by the addition or loss of groups of electrons of eight or a multiple of eight. This gives an almost absolute coincidence between calculated and observed values, and suggests that elements could be transmuted if we could extract a certain number of electrons from each atom. As there are several ways of extracting, say, one electron in a million, the prospect of transmutation, though very remote, is not hopeless.

ELECTRONIC RINGS

Sir J. J. Thomson's hypothesis of electronic rings is one of those fascinating conceptions which, like that of vortex atoms, "deserve to be true," even if they are not. Up to the present, they form the most profound speculation as to the inner structure of the atom, and they certainly suggest one possibility of accounting for the periodicity of the elements. To put it briefly, Thomson regards an atom as consisting of a number of electrons (not more than several hundred) contained within a larger "sphere of positive electrification," and held together by the positive charge distributed throughout the volume of the sphere. Such a mechanism, while difficult to conceive, has the advantage of accounting for the invariability of spectrum lines. The electrons are arranged in rings within the positive sphere. Experiments with floating magnets show that the arrangement of the rings depends upon the number of units (magnets or electrons) in a perfectly definite way. On adding unit after unit, the units arrange themselves in concentric rings, and certain combinations of numbers recur again and again in the inner rings, giving rise to a periodicity of similar arrangements as the number of units increases. Some of the rings are less stable than others, and, therefore, less likely to survive. In some arrangements of electrons, stability is increased by adding an electron, in others by subtracting one. The former constitute "electropositive" elements, the latter "electronegative." It cannot be said that the theory bears working out in any detail; but, so far, it is the only electrical theory of the atom which explains any of the periodic properties.

Sir W. Ramsay prefers to regard the electron itself as an atom of a substance properly called "electricity," this electricity being an element of very remarkable properties which combines with the positive atoms of the other elements to form neutral or ordinary atoms. On this theory, the only pure atoms we ever meet with are the particles which constitute "canal rays." The ordinary atoms are "electrides," or combinations of positive atoms with electricity. While Thomson inclines to interpret all elements in terms of electrons (which he calls "corpuscles"), Ramsay makes electricity an elementary substance.

CHAPTER XVIII

RADIOACTIVITY

WHEN Henri Becquerel discovered the uranium rays in 1896, he can hardly have been quite conscious of the immensity of the new field he was opening up for human exploration. Perhaps it is not correct to treat of radioactivity at all in a work on chemistry. For the new science which deals with it is, strictly speaking, not a chemical science. It is a kind of super-chemistry. Some would even call it alchemy, inasmuch as it deals with the transmutation of one elementary chemical substance into another.

But if radioactivity is excluded from chemistry, the field of the latter science is in danger of becoming seriously restricted—for nobody knows where exactly to draw the line between the two sciences. Besides the six radioactive substances, there are some seventeen transformation products more or less stable, but still, while they last, distinct chemical elements. Besides these, again, there are such elements as rubidium and potassium, which are slightly radioactive; and when we consider that one of the chief characteristics of radioactivity is the expulsion of positively charged atoms, electrons, and Röntgen rays, we are brought face to face with the fact that this characteristic is, under special circumstances, shared by all known elements except the so-called "inert," or "noble," gases recently discovered.

It is, therefore, impossible to say where exactly chemistry proper leaves off and radioactivity begins; and the difficulty of this distinction will be largely increased as soon as we begin to control the radioactive processes, and to use their enormous powers for the purpose of building up or destroying the chemical atom.

WHAT IS RADIOACTIVITY?

A substance is called "radioactive" when it spontaneously and continually emits rays capable of ionising gases. This "ionisation" consists in the breaking up of the molecules of the gas into ions, or particles having a positive or negative electric charge. It is discovered by the spontaneous discharge of an electroscope when immersed in the ionised gas, when the charge of the electroscope is neutralised by the charges of the opposite kind contained in the gas.

This is the usual test for radioactivity, and the simplest, though by no means the most striking. For a radioactive substance usually possesses other properties also. When strong enough, its rays produce a luminosity on a luminescent screen such as is used for demonstrating Röntgen rays. They also affect the photographic plate. And, lastly, their absorption raises the temperature of the absorbing body. When the rays are absorbed by the body itself, as happens when rays, coming from the interior, are absorbed by its outer layers, the radioactive body maintains itself permanently at a temperature above that of its surroundings. Thus, the radium preparations first examined by the Curies remained permanently at 3° C. above surrounding objects.

THREE TYPES OF RAYS

The rays emitted by radioactive bodies, sometimes called "Becquerel rays" after their discoverer, are not of a uniform constitution. They possess, in fact, widely different properties. Those which produce the greatest light- and heat-effects are called α-rays. They bear a positive charge, and consist of particles projected with speeds ranging from 8000 to 12,000 miles per second. They are stopped after traversing from 3 cm. to 7 cm. of air, and their ionising, phosphorescent, and photographic effects all have the same range.

A much more penetrating type of rays are the β-rays, which, like cathode rays, are capable of penetrating thin layers of aluminium, tin, and other metals.

In addition to these, Villard in 1900 discovered a third type of radiation, feeble indeed, but extraordinarily penetrating—in fact, the most penetrating radiation ever discovered, capable of traversing several inches of solid iron. This third type of rays is known as γ-rays.

Recent researches have shown that none of these rays are really new. The β-rays are simply the well-known cathode rays, described a generation ago by Sir W. Crookes under the prophetic name of "radiant matter." The only new feature about them is their extraordinary speed, which closely approaches that of light. The α-rays, on the other hand, are identical with the positively charged particles constituting Goldstein's "canal rays," obtained by perforating the cathode in a vacuum-tube. Lastly, the γ-rays are probably identical with Röntgen rays; but, again, of an extraordinarily enhanced and penetrating type.

These three types of rays present very distinct properties in a magnetic field. When the rays are emitted in a horizontal direction, and the lines of force of the magnetic field are vertical, the β-rays describe a horizontal circle, or portion of a circle; the α-rays are very slightly deflected in the opposite direction, and the γ-rays are not deflected at all. This is exactly the behaviour of cathode rays, canal rays, and Röntgen rays, respectively. But the new circumstance is that the older types of rays all require some source of power to maintain them, whereas the power of the Becquerel rays is derived from the internal energy of the atoms of the radioactive substance.

What is certain is that β-rays are simply electrons projected with very high velocities. That is to say, they are particles of infra-atomic size, whose mass is about $^1/_{2000}$ of that of a hydrogen atom, and whose electric charge is 4×10^{-10} of an "electrostatic" unit of electric quantity (i.e. a quantity which, when placed at a distance of 1 cm. from an equal quantity, repels it with a force of 1 dyne, or $^1/_{981}$ gram). It is also certain that the α-particles are atoms of matter, and most probably atoms of a gas called helium. What the γ-rays are is not yet quite certain. They may be ether-pulses, as the Röntgen rays are generally supposed to be. But another supposition, put forward by Bragg, is that they are "doublets" consisting of combinations of positively charged atoms with electrons. This would account for their possessing no apparent electric charge, and being undeflected in the magnetic field. Their penetrating character would then be accounted for by Bragg as follows: The absorption of charged particles is mostly due to their charge, which produces a violent commotion among the charges within the molecules of substances, and leads to a loss of kinetic energy, which is frittered away in the form of heat. Uncharged atoms projected with high velocities are not stopped in this way, as they produce no such electric commotion. The objection may be urged that ordinary atoms of matter might have similar penetrating power, being also in a state of violent motion due to heat. But the answer to this is that ordinary atoms in heat motion have speeds which are, on the average, about 10,000 times slower than the speed of α-particles, and that doublets of the kind imagined would, therefore, have a kinetic energy a hundred million times greater than atoms of ordinary matter. With such energy they might break down the atomic structures in their path, and tear their way through solid iron as a bullet would through tissue paper.

INTRA-ATOMIC ENERGY

It will be seen that in dealing with radioactive processes, we deal with sources of energy of an entirely new order. In 1905, Einstein, from considerations of the finite velocity of light and the energy embodied in a wave of light, concluded (see above, p. 148) that all matter is, so to speak, energy bottled up, that all inertia is the inertia of stored energy, and that when two masses attract each other, it is really their stores of internal energy which produce the attraction. As already mentioned, he estimated the amount of energy contained in a gram of matter, and found it to be 9×10^{20} ergs. Now, one gram of radium emits an energy amounting to 100 gram-calories per hour. One gram-calorie being equivalent to 42 million ergs, it would take something like 25 million years of such waste to dissipate the whole energy contained in the gram of radium. But, as a matter of fact, the rate at which energy is emitted by radium is constantly decreasing, though at such a low rate that after 1300 years it will still be found to be emitting half the energy it evolves now.

It is evident, then, that the enormous energy revealed in radioactive transformations by no means represents the total energy hidden within the atom. It is quite possible that even the total disintegration of a chemical atom into particles of the size and mass of an electron does not involve the dissipation of all its internal energy and the total destruction of its inertia. For even an electron possesses mass, and represents energy to an extent of at least a millionth of an erg. The facts already ascertained have exorcised the lugubrious threats of an inevitable decay of the energy of the visible universe. They have indicated a new and unlooked-for source of supply whence the available energy can be recruited. When the familiar natural forces fail, we may still draw on the infinite energies which well up out of the "infra-world," and who knows but that the infinite series of successive infinitesimal universes may harbour a supply of energy which guarantees an eternal existence and stability to the universe we live in!

RADIOACTIVE SUBSTANCES

The more or less permanent radioactive substances known up to the present are uranium, thorium, radium, actinium, polonium, ionium, and radio-lead. All these emit α-rays, except actinium and radio-lead, which are rayless. In addition to the rays, thorium, radium (and also actinium), give rise to a radioactive gas called an "emanation," which loses its powers remarkably quickly, dropping to half its energy in 3·7 seconds (actinium), 54 seconds (thorium), and 3·8 days (radium), respectively.

It is remarkable that radium, actinium, ionium, and polonium are entirely new chemical substances, whose discovery we owe solely to their radioactive properties, and chiefly to the ionising power of their rays. The value of this new and extremely delicate test for the existence of minute quantities of matter is strikingly shown in the investigations of the successive products of radioactive transformation carried out by Rutherford, Soddy, and others. Rutherford has performed the extraordinary feat of tracing the ionisation produced by a single α-ray particle—in other words, a single helium atom. Taken in conjunction with recent progress in the study of Brownian motions with the ultra-microscope, it means that we can henceforth deal with atomic and molecular individuals instead of aggregate masses.

RADIOACTIVE TRANSFORMATIONS

There is a certain parallelism between the amounts of uranium and radium contained in minerals. One ton of pitch-blende contains about 2 grains of radium, and three million times as much uranium. A few years ago an anomalous radium ore free from uranium was found at Issy l'Évêque. But the radium was evidently derived from a distant uranium lode by percolating water. In any case, it was confined to the surface of the mineral, and could be entirely dissolved away by acids which left the mineral unaffected.

The constancy of this ratio suggests that radium is evolved from uranium. But, so far, all attempts to find radium in uranium mineral containing none originally, and left to itself for several years, have failed. Boltwood has explained this failure as due to the existence of an intermediate product, which he calls "ionium," a product which is extracted with the radium. It is, therefore, useless to expect radium to be evolved direct from a pure uranium mineral.

Nor is the total activity found in uranium due to the metal itself. Crookes extracted from uranium a constituent which he called Uranium X, and which emitted all the β-rays, while the uranium only continued to emit α-rays. On observing the two substances separately for some time, uranium is found to recover, while Ur X decays. So that here again we have a clear case of parentage, or at least of ancestry, for Danne has recently discovered an intermediate product which he calls "radio-uranium."

The following genealogical table gives the whole series of changes undergone by uranium in its successive transformations, with the average life of each product:—

Uranium	7,500,000,000 years
Radio-uranium	?
Uranium X	32 days
Ionium	?
Radium	2500 years
Radium emanation (Niton)	5·3 days
Radium A	4·3 minutes
Radium B	38 minutes
Radium C	30·5 minutes
Radium D (Radio-lead)	17 years
Radium E_1	9·5 days
Radium E_2	7 days
Radium F	203 days

The last descendant, Radium F, is identical with Mme. Curie's polonium, which on further change probably becomes lead.

The Thorium series is given by McClung as follows:—

Thorium .	10,000 million years	Emanation .	54 seconds
Mesothorium$_1$.	5·5 years	Thorium A .	11 hours
Mesothorium$_2$.	6·2 hours	Thorium B .	1 hour
Radiothorium .	800 days	Thorium C .	?
Thorium X .	3·7 days	Thorium D .	?

And the Actinium series:—

Actinium . .	?	Actinium A .	36 minutes
Radioactinium .	19·5 days	Actinium B .	2·15 minutes
Actinium X .	10 days	Actinium C .	5·1 minutes
Emanation . .	3·7 seconds		

RADIUM AND GEOLOGY

The existence of radium in the rocks of the earth's crust has shed quite a new light on the controversy with regard to the possible age of the earth. The time required for geological changes at known rates is far in excess of the time during which, at the ordinary rate of cooling, the earth may have been a globe with a solid crust. But if, instead of starting with a limited supply of heat, the earth derives a continuous supply of energy from the internal store of radium, its geological evolution may be indefinitely prolonged.

The amount of radium found in rocks is amply sufficient to account for the whole of the earth's heat. Strutt has gone further than this, and proved that if the amount of radium found in accessible rocks is the same as that of deeper strata, the present gradient of heat is fully accounted for if the radium-bearing stratum is a shell only fifty miles thick. Joly has gone into this question very fully, and inclines to the opinion that the "catastrophic" changes of geology, the creasings and foldings of the earth's crust which build up mountains, may be accounted for by the unequal distribution of radium, which heats and weakens some parts of the earth's crust more than others.

A large sphere having a smaller area for its volume than a small sphere, a large sphere containing a certain amount of radium per unit volume will cool more slowly than a small sphere having the same amount of radium per unit volume. Hence it may well be that the heat of the planet is mostly due to radium. And that is why the moon is cold, the earth fairly warm, and Jupiter and Saturn probably at the boiling-point of water.

It is true that radium decays in a short time—a few thousand years at most. But it is ever renewed by its ancestor, uranium, and that again may be renewed after its career of 7500 million years by the formation of some yet denser substance (actinium?) which is so unstable that it rapidly disappears.

METALLIC RADIUM

In 1910 Madame Curie and A. Debierne performed the remarkable feat of obtaining radium in a pure metallic state. It was done by electrolysing radium chloride with an anode of iridised platinum and a mercury cathode. This gave an amalgam of radium, from which the mercury was driven off by heat in an atmosphere of hydrogen. The result was about a tenth of a grain of a brilliant white metal which turns black in air, burns paper, and dissolves rapidly and completely in water or dilute hydrochloric acid, thus showing that its oxide is soluble and that the mercury was really driven off.

SOLID EMANATION

Ramsay has succeeded not only in liquefying radium emanation, but in solidifying it under cold and pressure. The liquid emanation is colourless, and has a violet phosphorescence. The solid appears to burn with an intense blue light, which has suggested to him to rechristen it "Niton" instead of the original awkward and inappropriate name. Weighing it with Steele and Grant's micro-balance (described above), he found its atomic weight to be 222·5, which is as nearly as possible the value predicted by theory.

RADIOACTIVITY AND RARITY

If all elements were derived from each other by successive radioactive changes, proceeding from the greater to the lesser atomic weights, there will be an equilibrium between their respective amounts, those being more in evidence which survived longest, just as women have a permanent majority (in Europe) over men because their average life is longer. It may be that gold is rarer than silver simply because, when evolved, it has only a short life. If that is the case, it is, as Soddy has pointed out, hopeless to expect the sudden discovery of a great mountain of gold.

THE NEW ALCHEMY

Sir W. Ramsay and his assistants have been lately engaged in endeavouring to hasten radioactive changes, or to induce them in bodies which are not as a rule radioactive. Whether or not it is true that they have succeeded in transmuting copper into lithium—Madame Curie denies it—it appears certain that they have transmuted quite a number of elements into carbon. The elements so transmuted are silicon, zirconium, titanium, and thorium, all of which belong to the carbon group. This was done by conducting radium emanation into solutions of salts of these elements.

If this should turn out to be a genuine transmutation, we are indeed on the eve of a revolution which will remodel the whole of chemistry. If matter is energy, and transmuting matter is simply converting one form of energy into another, we may hope even in our own days to see some things achieved which will indeed change the face of the world. And those things are now being born in the flasks and tubes of our chemical research laboratories.

CHAPTER XIX

THE CHEMISTRY OF THE FUTURE

We have now traversed in rapid succession the whole field of modern chemistry. We have glanced at the kinetic theory of gases, the equilibrium between the various states of aggregation as regulated by the Phase Rule, the new science of Stereo-chemistry, the electrolytic theory of solutions, and the laws of osmotic pressure. We have studied the nature of affinity and valency, the velocities of ions, and the principles of modern analysis. We have become familiar with present-day views on crystallisation, on the rings and chains formed by carbon compounds, and on the connection between chemistry and the functions of life. We have noted the developments of metallurgy and chemical industry. And, finally, we have reviewed the present position of the atomic theory in the light of that latest and most pregnant of chemical phenomena, radioactivity.

In this rapid survey, one thing has stood out clearly: It is the priceless series of services which the conception of the chemical atom has rendered to the theory of chemistry. Without the atomic theory, and the Berzelius notation which embodies it, we should have no chemical formulæ and no scheme by which to arrange, classify, and catalogue the vast array of chemical facts issuing in a steady stream from the world's chemical laboratories. What the electron, or atom of electricity, is to modern electrical science, that, and more, is the chemical atom to the chemist.

The unparalleled series of triumphs achieved by the atomic theory during the nineteenth century has had the effect of enormously enhancing the prestige of the Daltonian atom. By a well-known psychological law, it has had the effect of exaggerating the real dignity and permanence of the atom. Ever anxious to find some refuge from the bewildering complexity of natural phenomena, the human mind lays hold of some conception which embodies the changelessness of a great class of objects and happenings, and pins its faith to that. But such changelessness, felt, in one mood, to be a welcome promise of repose, is, in another mood, felt to be an irksome restraint. The cloister has become a prison. No sooner have we discovered a natural law than we seek to escape from it—to transcend it. No sooner do we discover an indivisible atom than we seek to split it up.

PROBING THE ATOM

The ultra-microscope and the modern electroscope have proved capable of detecting the presence of a single molecule under certain circumstances. Brownian motions and radioactivity are the twin paths which converge upon the atoms. The chemistry of the future will become intimately acquainted with atoms and molecules. It will deal with them statistically. It will use them as bricks out of which to build up all known material structures. It will rely upon their average statistical properties, even as a statesman relies upon the average taste for tobacco, and the field-marshal relies upon the average physical courage of his soldiers.

That will be one consequence of our growing acquaintance with the Atom at Home. But there is another consequence of equal importance. There never has been an extension of human observational faculty but has revealed complexities unsuspected before. We simplify at one end; we complicate at the other. We unify phenomena under some great generalisation, and straightway we go and discover new worlds which do not fit into our scheme, and which wait for a later and yet wider generalisation.

There is no reason to believe that our experience in chemistry will differ from this general rule. No sooner shall we come face to face with the atom than it will show us a million different faces. This is no cause for alarm. It will not "shake the foundations of science." The new knowledge will come when humanity is ripe for it. If it comes too early, humanity will save its brain-power by quietly ignoring it. Facts will remain facts, whatever new facts are discovered, and those who prefer to regard atoms as perfectly hard, or perfectly elastic, identical granules, may rest assured that that view covers all but an insignificant number of the facts of chemistry known up to the present.

ARE ATOMS ALIKE?

But evidence against the sameness of the atoms of a given body is steadily accumulating. Certain facts connected with the ionisation of a gas by Röntgen rays, and the discharge of metals by ultra-violet light, tend to show that either (*a*) light consists of discrete elements—we might almost say atoms of light; or (*b*) that atoms of the same substance are not precisely alike. But that is not all. We know that the speeds of atoms and molecules differ. Some of them move faster than others. The ultra-microscope actually allows us to see this. Now, according to modern electromagnetic theory, the inertia (or mass) of a charged body depends to some extent upon its speed, becoming enormously greater than its normal mass when that speed approaches the velocity of light. Therefore the atoms of an ionised gas certainly differ from one another in mass. But they differ in other particulars also. When a gas becomes incandescent, probably not more than one atom in 10,000 is actually emitting the observed spectrum at any given time.

This means that one atom may be issuing radiant energy while the others are comparatively quiescent. This implies a greater difference of configuration and of internal structure than even the difference of mass just referred to.

In radioactive bodies the difference between the active and the quiescent atoms is enormous. It is the difference between a shell before explosion and after. But one, at all events, of the processes of radioactivity is proceeding wherever an electric current passes. Even in the interior of a metallic conductor, electrons (or, in other words, the β-rays of radium) are being expelled from some atoms and absorbed by others.

This exchange of electrons is the basis of all chemical reactions. These very chemical reactions, whose quantitative relations irresistibly suggest the sameness of atoms—at least when they are taken in sets of half a trillion at a time—are conditioned by the partial disintegration of those same atoms. When we come to deal with atoms as individuals, our chemical equations may no longer remain strictly valid; but we shall learn much of that which now appears baffling and unaccountable, and any loss of initial simplicity will be amply compensated by the unravelling of problems hitherto insoluble.

THE ELEMENTS AS LIVING SPECIES

The view that a molecule of water consists of two identical atoms of hydrogen and one atom of oxygen stuck together, or in orbital motion, may satisfy certain elementary observations of chemistry; but as an image it implies too much in one way and too little in another. It implies a simplicity and stability which probably does not exist, and it accounts in no way for the forces which are supposed to bind the atoms together. The physicist is bound to probe more deeply. "The physicist," says Larmor, "is never likely to forget that any simple piece of matter is a vast interlacing, interdependent complex, which he can never hope completely to disentangle or resolve: he is certain that matter is of grained structure, but to him the grains are very far from being mutually isolated things—each of them is actively influenced by all the others around it. Yet he has no alternative but to hold that each ultimate grain is itself a self-existing cosmos, of complexity probably beyond any complete analysis on our part, which may indeed to appearance merge itself in combination with another atom or molecule, but is always recoverable unaltered—that there is no degradation of matter. He holds probably that it is necessary to believe that in the same pure substance the molecules are all exactly alike, or, at any rate, that they are as nearly alike as individuals of a very sharply defined species in the organic world; though he knows no natural reason which would compel them to be so constituted, except in so far as they may represent the limited number of types of dynamical structures that can be built up from simpler identical primordial elements."

That the molecules of the same elementary substance are "*as nearly alike as individuals of a very sharply defined species in the organic world*" is what the chemistry of the future will have to content itself with. It will take it as a limitation sufficient for large-scale chemical processes. It will also take it as a declaration of freedom which gives all the gorgeous colouring of animated nature to the hitherto barren and lifeless world of atoms.

THE LIFE OF ATOMS

The microscope and its histological revelations introduced us to the individual life of the cell. It is quite possible that the ultra-microscope and its molecular revelations may introduce us to the individual life of the atom. The volume of the cell is to the volume of the human body as the latter is to the volume of the earth. Both ratios are as 1 : 10^{22}, approximately. No living cell contains less than 100 million atoms. The atom will probably be found to play much the same part in cell life as the cell plays in the animal body. But the specialisation will be more narrowly determined. The cell recruits itself by absorbing suitable foodstuffs through its walls. How does the atom recruit itself, or does it recruit itself at all?

This we know: that every atom constantly gives out energy to its surroundings, and takes it up again from them. This exchange is usually carried on in the way of radiant heat. The average energy contained in an atom of the same substance is a constant quantity, unless it happens to be in a state of radioactive disintegration. Is that not very nearly all we can say of the living cell? The cell strives by every means to maintain its internal energy. When that internal energy falls below a certain minimum, disintegration results. Some cells offer a greater resistance to this disintegration than others. These are the cells whose internal energy is more potential than kinetic, and less liable to be radiated away.

If, as has been recently maintained, matter is stored energy, then atoms may with justice be said to "feed" on the energy they receive from outside, and which is necessary to enable them to radiate it out again as they do.

There remain the questions of death and reproduction. These cannot be solved satisfactorily unless we can follow up an individual atom and note all its changes, if such there are. A radioactive particle cannot be followed up, for we can only perceive it when it moves at a speed comparable with the speed of light—a speed we cannot follow to any great distance. The ultra-microscope offers a possibility of following up some of the larger molecules, like those of sugar, but the atom is still quite beyond its powers. At the present time, therefore, we cannot detect the life of the individual atoms. We can only deal with large sets of atoms. That being so, the question of the reproduction of an atomic species must be attacked along statistical lines. We then find that a lump of a particular metal, left to itself for any measurable length of time, appears to contain the same number of atoms as before—say within one part in a hundred million, which represents nearly the utmost attainable accuracy of weighing. The atoms we find at the end of the long time interval may either be identically the same as they were at the beginning, or they may be descendants of these, having taken their place on the death of their forerunners. In order that this may be in accordance with observed facts, the number of descendants must be the same as the number of ancestors, within one part in a hundred million. There must, in fact, be equilibrium between the birth-rate and death-rate of atoms.

Such equilibrium is not unknown in the organic world. A naturalist may calculate with some certainty the relative numbers of given species in a pond whose average temperature and whose soil are known. These numbers are constant or but slightly fluctuating, the surplus of one species being counterbalanced by the excessive growth of a species hostile to it.

There are many more parallelisms between atomic phenomena and cell-life. The striking, and as yet unexplained, contrast between the large and heavy positive atom and the minute electron is a fairly general rule in organic life, where the female individual is larger and less mobile than the male. The "attraction" between the two sexes is paralleled by that between positive and negative electricity, and both kinds of attraction are responsible for the most momentous results of their respective worlds.

Mendeleeff's periodic system of atomic weights may harbour a greater truth than any yet suspected. Who knows but that the rows or columns represent each a single species in various stages of growth or decay? Some chemical reactions, which we take as separating distinct chemical species, may also be interpreted as separating those individuals of the same species which have reached a certain stage of development. The rarest elements will be those whose state is the most transitory. Many elements are so transitory that they are never present in sufficient quantity to be discovered at all.

CHEMISTRY AS A BRANCH OF BIOLOGY

Chemistry thus appears to be ready to split up into two already existing sciences. Physics is disposed to absorb the large-scale phenomena, while biology will probably in the end annex the phenomena of atomic proportions. A chemical substance will be regarded as a continuous body having certain physical properties. That will suffice for the mechanical and physical utilisation of the substance. When the same substance is regarded as a collection of atoms, it will probably in the distant future be dealt with according to biological laws. The debatable ground between the two sciences will be occupied by the remains of what is now called chemistry. This tripartite division will give us the maximum power of dealing with chemical properties, and these will come more and more under our control.

Of the two sciences, chemistry and biology, the latter is the more profound, the more ultimate. A chemical explanation of life is no explanation, since it reduces something which we do know in ourselves, viz. life, to something with which we can never become acquainted, viz. dead matter. Could we reach matter in a way which does not involve our own sensations, things would be different. But the living sense-organ always comes in somewhere, and while we are sure that our sensations are real, every other reality is purely a matter of faith, or conjecture, or probability.

If, therefore, we want ultimate things, we must take the phenomena of life. But for many days to come, practical chemists will be content to achieve success with the proximate things before them, leaving the unravelling of their inner meaning to a future generation.

THE END

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